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Degradation of soils and micaceous minerals by the removal of potassium with sodium tetraphenylboron

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DEGRADATION OF SOILS AND MICACEOUS MINERALS BY THE REMOVAL OF POTASSIUM WITH SODIUM TETRAPHENYLBORON

by

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INTRODUCTION

K occurs in soils in water-soluble, exchangeable, fixed, and lattice forms. The term lattice K is used here in reference to K that has never been disturbed from the crystal lattice of K-bearing minerals in the soil. Fixed K on the other hand is added K that is adsorbed so strongly that it is not readily replaced with neutral salts. Most of the fixed K is located between the layers of a contracted micaceous mineral lattice in a position comparable to lattice K in these minerals. Therefore, it is often difficult to distinguish between lattice and fixed forms, and the term non-exchangeable K is sometimes used to include both.

Only the water-soluble and exchangeable forms of K are readily available to plants. When these forms are depleted by cropping, a release of non-exchangeable K occurs. That is, some of the fixed and lattice K is shifted to exchangeable positions, where it is available to plants. The continued K-supplying power of a soil, therefore, depends upon this process of release.

One of the main processes by which K is released is the replacement of K in the contracted lattice of micaceous minerals in the soil with hydrated cations such as Ca, which cause the layers of the lattice to expand. When this occurs, the mineral is said to be degraded. Thus, the process it-

self will be referred to as the degradation of micaceous minerals. This term may be applied loosely to soil also, but in this case it actually applies to the micaceous minerals in the soil.

Since the degradation of micaceous minerals actually involves nothing more than the replacement of fixed or lattice K in these minerals, it should be governed by the same factors that have been found important in the release of any fixable cation. It has been found that the removal of fixed NH_4 is restricted by the presence of fixable cations in the extracting solution. Therefore, it is to be expected that, in the degradation of micaceous minerals, the K release will, in a like manner, be influenced by the concentration of soluble and exchangeable K present. The level of these forms is constantly fluctuating, decreasing with cropping and increasing with K release. Thus, to evaluate the ability of a soil to release K, these forms must be maintained at some constant level. If the soluble and exchangeable K are removed completely, and no released K is allowed to accumulate, then the release of K from micaceous minerals should proceed at a maximum rate. Under these conditions, it should be possible to validly compare soils with regard to their K-supplying power.

Fortunately a new compound, sodium tetraphenylboron (NaTPB), is now available which will precipitate K and not

the other cations commonly found in soil such as Ca, Mg, and Na. With this compound it should be possible to keep the soluble and exchangeable K levels extremely low, without causing the wholesale removal of the other cations which so often characterizes K release studies in soils and minerals. Information on the use of NaTPB is, however, limited. Therefore, the primary objective of this thesis has been to develop methods of using NaTPB in soils and clay minerals.

In this study it was necessary to determine the optimum conditions for K precipitation, to develop methods of removing the precipitated K, and then to determine the K in the KTPB compound. Some degradation experiments with soils and clay minerals were carried out with the methods available to determine whether a further investigation of this nature was warranted.

LITERATURE REVIEW

Forms of Soil K

Hissink (33) is generally credited with having been the first person to report that an equilibrium exists among the various forms of soil K. The nature of this equilibrium and its importance have since been studied by several investigators (13, 42, 60, 63).

Several expressions have been used to depict the equilibrium that exists among the various forms of K in the soil. Probably the most common expression encountered is that proposed by Peech and Bradfield (42):

Non-exchangeable $\rightleftharpoons$ exchangeable $\rightleftharpoons$ water-soluble.

Other investigators, however, have tried to specify more precisely the non-exchangeable K involved in this equilibrium. Wiklander (60) expressed the equilibrium as:

lattice $\rightleftharpoons$ fixed $\rightleftharpoons$ exchangeable $\rightleftharpoons$ water-soluble,

while Wood and DeTurk (63) used the more elaborate expression:

primary mineral
$\searrow$
fixed (acid-insoluble $=$ acid-soluble)
$\searrow\searrow$
replaceable
$\searrow\searrow$
water-soluble.

In each case, these expressions show the essential fact that there will be a release of K to exchangeable and soluble forms if these forms should be decreased. To understand

where this K comes from, however, requires a more careful definition of the forms of K in soil.

In a recent review of the forms of K in soil Wiklander (60) arbitrarily divided soil K into four categories: water-soluble, exchangeable, fixed, and lattice or native K. The fixed and lattice K forms are of particular interest, because they constitute the reserve supply of K in the soil. Fixed K may be defined as added K that is not readily removed by neutral salts (38). Lattice K, on the other hand, may be defined, by generalizing Barshad's (8) use of the term "native K", as the K that has never been disturbed from its naturally occurring position in the crystal lattice of K-bearing minerals. In this manner a distinction can be made between these forms by definition, but in practice this distinction is not readily made. For this reason, the fixed and lattice K are often classified together as non-exchangeable K.

It is generally agreed that fixed and lattice K occupy the same position in micaceous minerals (6, 41, 57). Thus, a comparison of one micaceous mineral that contains fixed K with another that contains lattice K may reveal little difference in properties. Barshad (6), for instance, found that the properties of K-saturated vermiculite closely approximated those of ordinary biotite, even though the K in the vermiculite was fixed, while the K in the biotite was lattice K.

This distinction is also confused by the fact that decaying plant material is always returning K to the soil, where it may be fixed. Thus, an investigation of the release of naturally occurring K in the soil will encounter release from fixed and lattice forms even though no direct application of K was made. It is essential, however, that every effort be made to distinguish between these forms, because it has now been found that fixed K is more easily replaced than native K in micaceous minerals (8).

K Fixation

To understand the process of K release in soils, it is first necessary to comprehend the nature of the various forms from which K is released. Fixed K is one of these forms.

That soluble K applied to soils can be fixed was discovered by Dyer (17) and confirmed by Frear and Erb (23). Following these early observations of K fixation, it has become increasingly evident that much of the fixation and subsequent release of K is associated with the montmorillonite and illite in the soil (41, 48, 52, 55, 57). More recently it has been emphasized that vermiculite-type minerals are also responsible for K fixation in soil (1, 9, 37).

To characterize the mechanism of K fixation in expanding lattice clays, Truog and Jones (55) and Wear and White (57) showed that bentonite (montmorillonite), on fixing K, suffers

a decrease in exchange capacity comparable to the amount of K fixed. Thereby, for this mineral, it was shown that K fixation involves the trapping of K in interlayer exchange positions.

Barshad (6-9) and Gruner (28) have studied this aspect in greater detail with other micaceous minerals. When vermiculite was saturated with K or NH_4, it was found that the lattice of the clay was contracted to 10.1Å and 10.3Å, respectively, and that this spacing was retained when the vermiculite was immersed in water. Thus, the effect of fixable cations (K and NH_4) in solution is to cause or retain a contracted lattice spacing, thereby trapping ions held on exchange positions between the plates. On the other hand, hydrated ions, such as Na and Ca, on entering the edges of the clay plates in number, effect an expansion of the plates and subsequently displace cations fixed or trapped between the plates.

This experimental work has helped to show the process whereby K is held in and released from lattice spaces between micaceous clay plates. It indicates the role of hydrated cations in this release as contrasted with the retarding or preventive action of soluble fixable ions. For a more detailed presentation of work on fixation in micaceous minerals one is referred to the literature reviews by Reitemeier (45) and Hanway (30).

Degradation of Micaceous Minerals

While there have been several reports as to the identification of end-products in the degradation of micaceous minerals, characterization of both initial products and degradation end-products has in many cases been sketchy and incomplete. Nevertheless, various field studies and laboratory degradation investigations do give an insight into the processes of natural and artificial degradation of micaceous minerals.

The degradation of mica to vermiculite and the reverse synthesis of vermiculite to mica have been reported in several instances. Walker (56) in dealing with soil clays of Scotland, observed that a biotite-like mica, on weathering, assumes the c-axis spacing of vermiculite. His work also indicated that montmorillonite may be a product of mica degradation. Caillére et al. (14) found that boiling of phlogopite with $MgCl_2$ resulted in the formation of vermiculite and that the boiling of muscovite and illite with $CaCl_2$ produced "expanded" lattice minerals. Barshad (6) found that leaching of hydrobiotite and biotite with $MgCl_2$ resulted in the eventual formation of, respectively, vermiculite and a vermiculite-like material (the latter product being similar to vermiculite in regard to x-ray diffraction pattern and water content).

It appears that micas may degrade not only to vermiculite

but also to hydrated micas (which Barshad says are interleaved combinations of mica and montmorillonite or vermiculite), and to montmorillonite (12, 56). Jackson et al. (34) and White (58) found that illite degrades through a "mica intermediate" phase to montmorillonite.

In a comparison of biotite with muscovite Denison et al. (16) noted that biotite tends to weather more than does muscovite and that the former eventually assumes a relatively stable product of about 4% K_2O. They considered that the weathering process involves loss of K and Mg and gain (relatively) in Al_2O_3 and water, with the loss in K_2O equivalent to the gain in water in the case of muscovite. More recently it has been shown that the replacement of K from micaceous minerals depends on the use of replacing cations that are still hydrated when they are adsorbed on the mineral (9, 31).

In the study of the degradation of fixed K, workers frequently have observed the reluctance of fixed K to enter solutions which already contain a fixable ion. In this regard Wiklander (59) obtained only 5% of the potential exchange between K^{42} and K fixed on illite. Merwin and Peech (38) observed that fixed K tended to be freed to the exchangeable form only when exchangeable K had been leached from soil by cations that are not fixed by the soil. When NH_4 was used as the replacing cation, the fixed K was

not released. Hanway (30, 31) reported the "blocking" of fixed NH_4 from release to solutions containing small amounts of soluble K or NH4. Hanway proposed that a very small concentration of fixable cation, in the face of large concentrations of hydrated cation, prevented the expansion of the micaceous mineral crystal lattice.

Wear and White (57) attempted to remove an end-product of degradation, soluble K, in order to speed the degradation of illite. Thus they removed K as it entered solution by precipitation as the cobaltinitrite. This precipitation method, in combination with a $MgCl_2$ treatment, removed more K than did a $MgCl_2$ treatment alone and resulted in the partial degradation of the illite to montmorillonite.

In pursuing the idea of removing blocking (fixable) cations from solution so as to efficiently degrade illite, Hanway (30) employed a new precipitant, sodium tetraphenylboron (NaTPB), to remove these cations from solution. By boiling illite with NaTPB in a salt solution he was able to degrade the illite to a much greater degree than was the case with boiling without NaTPB.

In light of Hanway's results, it seemed probable that degradation of micaceous minerals could be markedly accelerated by the continuous removal from solution (precipitation) of K solubilized through degradation. Thus there would be no free K to interfere with further release by replaceable

(hydrated) cations.

Tetraphenylboron Compounds

K determination by TPB compounds

Until recently K has been commonly determined by precipitation as the perchlorate, cobaltinitrite, or chloroplatinate precipitate; by colorimetric methods; or by flame photometry. Then, in 1949, Wittig et al. (61) discovered the specificity of the precipitation, in dilute acid or in neutral solution, of K, NH_4, Cs, Rb, and N bases by NaTPB. Since that time many investigators (11, 15, 19, 36, 44, 46, 47, 51) have devised and improved various methods for the determination of K through the use of TPB compounds.

Most of the earlier methods for the determination of K with TPB compounds were gravimetric procedures in which KTPB was weighed (11, 15, 19, 36, 51). Flaschka et al. (21) developed a gravimetric method in which KBO_2 was formed by the heating of KTPB and was then weighed (or was titrated with standard HCl or NaOH). They also devised a method whereby KTPB was dissolved in a standard base containing $HgCl_2$ (20). Acid liberated by the reaction of TPB ions with mercuric ions was measured by titrating the base remaining after the reaction.

Other procedures involving titration following precipitations of K as KTPB were reported by Rüdorff and Zannier

(46) and Spier (50). Rüdorff and Zannier dissolved KTPB in acetone and titrated the TPB ion with $AgNO_3$ solution. Since AgTPB is insoluble in acetone, the TPB ion is precipitated from solution as AgTPB. Spier, on the other hand, employed an empirical oxidation of TPB in KTPB, using ceric ion.

Various instrumental methods of analysis have been reported, but none have found general application. Kemula and Kornacki (35) determined excess NaTPB by an amperometric titration with $TlNO_3$. Findeis and De Vries (18) used a recording polarograph in the determination of KTPB. Raff and Brotz (44) were able to determine K by a conductimetric titration with LiTPB, provided Na and alkaline earths were at a minimum.

For reviews of methods for determining K by TPB compounds one is referred to Gloss (26), Belcher and Wilson (10, pp. 260-266), Nutten (40), and Sykes (53, 54). Comprehensive bibliographies of the literature on TPB compounds have been prepared by Barnard (3, 4, 5).

Preparation of TPB compounds

According to Wittig and co-workers (61, 62), TPB compounds may be prepared either by a Grignard procedure or by a reaction of BF_4 with C_6H_5Li:

$$BF_3 + 4C_6H_5MgBr \rightarrow [B(C_6H_5)_4]MgBr + 3MgBrF$$

$$2[B(C_6H_5)_4]MgBr + Na_2CO_3 \rightarrow 2Na[B(C_6H_5)_4] + MgCO_3 + MgBr_2$$

$$BF_4 + 4C_6H_5Li \rightarrow Li[B(C_6H_5)_4] + 3LiF$$

Solubility of TPB compounds

LiTPB and NaTPB are both very soluble in water. K, Rb, Cs, NH_4, amines, Ag, and heavy metals (Tl) form insoluble TPB compounds (51, 61, 62). The difference in solubility between the Na compound and the K compound is so marked that one can determine 20 mg. K in the presence of as much as 2 gm. of Na.

Raff and Brotz (44), using a visual turbidity comparison with AgCl, estimated the solubility of KTPB as less than 4×10^{-3} mg. K per 100 ml. of water. Geilmann and Gebauhr (25), measuring radioactive count of K^{42} in solution, arrived at the more generally accepted figure of 1.5×10^{-4} mole per liter at 20° C. (0.578 mg. K per 100 ml.; $K_{SP} = 2.3 \times 10^{-8}$).

Both KTPB and NH_4TPB are soluble in acetone (20, 46, 61). Rüdorff and Zannier (46) recommended that, for a particular Volhard titration of KTPB, the KTPB be dissolved in 40 ml. acetone per gram of KTPB. Findeis and De Vries (18) reported the ready solubility of KTPB in N, N'-dimethylformamide.

Rapidity of solution of KTPB varies according to size of precipitate particle. Geilmann and Gebauhr (25) found that washing fine-grained KTPB with dilute HOAc and with NaTPB-

containing dilute HOAc resulted in the solution of, respectively, 5.24 ppm (52.4 micrograms) and 0.06 ppm (0.6 micrograms) K. When large-grain KTPB crystallized from acetone was washed with the same solutions, 40.6 micrograms and 0.2 micrograms K, respectively, were dissolved.

Stability of TPB compounds

Gloss and Olson (27) found that storing for a few weeks at pH 3 resulted in considerable decomposition of NaTPB solution. At pH 5 and pH 7 the storing of a 0.6% NaTPB solution for 84 days resulted in no marked decomposition in the solution.

HCl and other acids are capable of hydrolyzing LiTPB or NaTPB (25, 61). At room temperature Cluley (15) found hydrolysis of TPB compounds during the precipitation of KTPB in 0.1 N HCl solution but not in 0.01 N HCl. Sporek and Williams (51) likewise observed decomposition during precipitation at room temperature in 0.2 N HCl, but reported no decomposition in the same strength acid at 0° C.

Geilmann and Gebauhr (25), on heating alkali TPB precipitates at 150° C. and 200° C. for one hour, determined losses of 0.25% to 0.50% in weight at the lower temperature and 0.75% to 1.0% at the higher temperature. Thus both high temperature and low pH are seen to reduce the stability of TPB compounds.

Decomposition and oxidation of TPB compounds

Wittig et al. (61) reported that $HgCl_2$ would decompose KTPB in methyl alcohol solution, according to the following reaction:

$$K[B(C_6H_5)_4] + 4HgCl_2 + 3H_2O \longrightarrow 4C_6H_5HgCl + KCl + 3HCl + H_3BO_3$$

Flaschka et al. (20) obtained the same reaction in basic solution. They measured the boric acid released as an indirect determination of K.

Spier (50) employed ceric ammonium nitrate to oxidize the phenyl rings in KTPB. According to the conditions of his procedure he found that he consistently effected only 60% of the potential oxidation of the phenyl rings.

K precipitation by TPB compounds

It is generally believed that there should be 5 to 20 mg. of K_2O per 100 ml. in the precipitating solution for optimum precipitating conditions (11, 15, 36). Cluley (15) obtained quantitative precipitation of as little as 1 mg. of K_2O in 100 ml. at pH 2 and at pH 6.5. He reported errors of about 7% when precipitating 0.63 mg. and 0.32 mg. of K_2O at pH 6.5 and higher errors (16% and 82%) when precipitating the same amounts at pH 2. In all cases he used 8 ml. of 3.4% NaTPB as the precipitant. Thus, a known amount of K should be added to any solution containing less than 1 mg. of K_2O per

100 ml. of solution if a precise K_2O analysis of the solution is to be made. For the precipitation of K in the presence of NH_4 or Ca, Berkhout (11) found that at least 10 mg. of K_2O per 100 ml. should be present.

K has been precipitated as KTPB over a wide range of pH conditions. To form large KTPB crystals Kohler (36) precipitated KTPB in a pH range of pH 1 to 1.5, at room temperature. On the other hand, Sporek and Williams (51) and Cluley (15) obtained large errors due to TPB hydrolysis under these conditions. Cluley recommended use of 0.01 N HCl at room temperature, while Sporek and Williams obtained satisfactory results with 0.2 N HCl solutions at 0° C. For low concentrations of K (1 mg. K_2O per 100 ml.) Cluley obtained much lower errors with a precipitation at pH 6.5 than at pH 2.0.

In separation of K from NH_4 and Ca through use of EDTA and formalin, Berkhout (11) utilized a solution just alkaline to phenolphthalein. Rüdorff and Zannier (47) employed a much more strongly alkaline reaction (near pH 14) for a similar separation of K from NH_4.

Flaschka (19) and Rüdorff and Zannier (46) recommended pHs of 4 to 6 and 5 to 6, respectively, with precipitation taking place at 60° to 80° C. so as to increase particle size of the precipitate.

Geilmann and Gebauhr (25) found that the error due to the decomposition of TPB compounds increased from 1% at pH

2.5 to 2.5% at pH 1, when precipitation was conducted at room temperature. Following precipitation of KTPB in acid solutions they found 0.45% of the added K remaining in solution at pH 1 and 0.2% at pH 2.5 to 5.5.

Temperatures recommended for the precipitation of KTPB have ranged from 0° C. to higher than 60° C. While Kohler (36) recommended precipitation in dilute mineral acid (pH 1 to 1.5) at room temperature, and Gloss (26) concurred in the recommendation, Sporek and Williams (51) suggested that 0° C. would be necessary if one is to use such an acid medium without suffering undue decomposition of precipitant and precipitate. Rüdorff and Zannier (46) and Flaschka (19) believed that precipitation at higher pHs (4 to 6) required 60° to 80° C. temperatures to insure adequate particle size. Geilmann and Gebauhr observed large errors in their K determinations when the precipitation was carried out at 50° to 70° C. in the pH range of 3.5 to 5. Their results, however, are not consistent with other results obtained by other investigators.

Little direct study has been made of the amount of excess precipitant required under various conditions of precipitation. Geilmann and Gebauhr found that excess precipitant concentrations of 0.1% to 0.3% in the precipitating liquid are adequate for complete separation of even small amounts of K from 100 ml. of solution. Schwaibold and Kohler (49) considered that an excess of about 0.04% precipitant

(based on weight of solution) is sufficient (when this amount represents 50% in excess of that required to precipitate the K). Berkhout (11) used excess precipitant concentrations of about 0.1% to 0.2% (1- to 3-fold excess).

Data are not consistent enough to indicate the error one may expect from use of an insufficient excess of reagent. One might conclude that a concentration of excess precipitant of 0.05% to 0.1% in the precipitating solution would be sufficient to effect quantitative K precipitation, provided the amount of precipitant present exceeds the K to be precipitated by 50%.

Conditions for solution of KTPB

Wittig et al. (61, 62) observed that KTPB is soluble in acetone. Most methods involving the solution of KTPB have employed acetone or acetone-water solution as solvent. Findeis and De Vries (18) found KTPB readily soluble in N, N'-dimethylformamide.

It was observed by Rüdorff and Zannier (46) that KTPB dissolved in acetone reacts, in a titration with $AgNO_3$, as if the KTPB were ionized. As further indication of the ionization of KTPB in acetone, Flaschka and Sadek (22) were able to determine K indirectly by passing a KTPB-acetone solution through a H-saturated exchange resin column. H measured in the TPB-acetone eluate was equivalent to K added

originally.

Data as to the effect of the acetone-water ratio on the solubility of KTPB in an acetone-water system have not been available. Experimental methods have generally involved the use of 1:1 or higher ratios (by volume) of acetone to water.

MATERIALS AND METHODS

Materials

Sodium tetraphenylboron (NaTPB)

In early work on experimental methods the "PotassiVer" brand of NaTPB manufactured by Hach Chemical Company, Ames, Iowa, was used. Because of difficulty in obtaining "PotassiVer" free of decomposition products, Baker's "Reagent" grade of NaTPB was used in later work.

"PotassiVer" solutions were clarified before use according to a slight modification of the method recommended by the manufacturer (29, p. 20). For each 100 ml. of 3.4% solution desired, 0.25 gm. of $AlCl_3 \cdot 6H_2O$ and one drop of 0.5% phenolphthalein were dissolved in about 70 ml. of water. Three and forty-five hundredths gm. of "PotassiVer" were dissolved in the solution. Then 10% NaOH was added to the point of a pink phenolphthalein color. After standing for 5 minutes the solution was filtered and adjusted to pH 7.0 $\pm$ 0.5 by dilute HCl. The solution was then made to volume and used within a few days.

The above clarification procedure was used in the preparation of solutions from Baker's NaTPB in the study of experimental methods. During the actual degradation of soils and micaceous minerals several comparisons were made between TPB solutions so prepared and solutions prepared without

such clarification. In each case there was no effect from the aluminum hydroxide treatment. Therefore, solutions used in most degradations were not so treated. Where large amounts of precipitant were required, weighed amounts of the dry precipitant powder were added directly to the degradation system.

Sodium tetraphenylboron, $Na[B(C_6H_5)_4]$, has an equivalent weight of 342.2. Thus, the 3.4% NaTPB solution commonly used is a 0.1 N reagent. One and three-tenths ml. of this 3.4% NaTPB solution (0.13 me.) are chemically equivalent to 5.0 mg. (0.13 me.) of K.

Minerals and soils

Muscovite and biotite samples were obtained from Ward's Natural Science Establishment, Rochester, New York. The muscovite contained 0.042% exchangeable K (1.07 me. per gm.), as determined by neutral N NH_4OAc, and 8.74% total K, as determined by J. Lawrence Smith fusion. The biotite contained 0.023% exchangeable K (0.58 me. per gm.) and 7.70% total K.

The vermiculite sample used in this problem was obtained from the Zonolite Company, Evanston, Illinois. It was characterized by the company as being a "high exchange capacity ore from South Carolina mines." The vermiculite contained 0.019% exchangeable K (0.49 me. per 100 gm.) and 2.80% total

K.

Both the micas and the vermiculite were ground in a Christy-Norris laboratory hammer mill, using a screen with round holes 1/16 inch in diameter.

The illite used was a Goose Lake Grundite obtained from the Illinois Clay Products Co., Joliet, Ill. It was fine enough to easily pass a 20-mesh screen.

Soils tested were a Fayette silt loam from Dubuque County, Iowa, and a Carrington silt loam from Delaware County, Iowa. Both samples were taken from the surface 6 inches of their respective profiles. They were ground so as to pass a 20-mesh screen prior to use.

Resins

Two exchange resins produced by the Rohm and Haas Company, Philadelphia, Pennsylvania, were used in this work: "Amberlite IR-120", a strong cation exchange resin of the polystyrene nuclear sulfonic acid type, possessing an exchange capacity of 4.25 me. per gm.; and "Amberlite IRA-410", a strong anion exchange resin of the polystyrene quartenary amine type, having an exchange capcity of 3 me. per gm.

"Amberlite IR-120" will henceforth be designated as "IR-120", with "Na-IR-120" designating a Na-saturated "Amberlite IR-120" and "H-IR-120" a H-saturated resin. Saturation of the IR-120 resin was effected by leaching the

resin with an amount of concentrated HCl or NaCl solution equivalent to 20 times the exchange capacity of the resin. The resin was washed with water until the eluate was free of chlorides and was then air dried.

Solutions

A NaOAc-HOAc solution which is loosely referred to as Morgan's solution for simplicity's sake was used in this work. Unlike the "universal extractant" advocated by Morgan (39), which is 0.52 N to HOAc and 0.73 N to NaOAc, this solution is equimolar with respect to HOAc and NaOAc. However, it is like Morgan's extractant in that it is strongly buffered at a pH of about 4.8. The normality of this solution is expressed on the basis of total acetate concentration.

Methods

All analyses for K in aqueous solutions were made with a Perkin-Elmer Model 52-C or 52-A flame photometer, using LiCl as an internal standard. Experimental data reported in this thesis represent average values for duplicate samples, except where otherwise noted.

One phase of this investigation has dealt with methods for determining K in KTPB. In all other cases, unless indicated to the contrary, analyses for K in KTPB were effected

through hydrolysis by aqua regia. The detailed procedure for determining K in KTPB through hydrolysis by aqua regia is as follows.

To remove salts other than KTPB, wash the dried precipitate with a 0.034% NaTPB solution, stirring the precipitate with a rod occasionally and decanting the wash solution into a medium porosity Pyrex sintered glass Buchner funnel. Rinse the precipitate in the beaker and funnel with 5 ml. of water. Discard the wash water, and, using acetone, wash the precipitate from the beaker and funnel into the filter flask. Transfer the dissolved KTPB to a beaker, and again take the solution to dryness on a steam plate. If much KTPB adheres to the beaker wall, wash the wall with 1:1 acetone-water, and again evaporate the KTPB to dryness.

Add aqua regia, cover the beaker with a watch glass, and place the beaker on a warm hot plate. Once the brown fumes within the beaker have cleared away, heat the beaker on a steam plate for at least 2 hours. At the end of this period wash the watch glass and beaker sides, and dilute the solution to about 80 ml. with hot water. Filter the hydrolyzate through a conical Whatman No. 42 filter paper into a 400-ml. beaker, and wash the hydrolyzed residue with hot 0.01 N HCl.

Dry the filtrate on a steam plate to remove the aqua regia. Add a few drops of 0.1 N HCl, followed by 50 ml. of

water, to the residue, and allow the solution to digest for 15 minutes on a steam plate. Filter the solution, and wash the beaker and paper with water.

Add enough LiCl to the filtrate to insure a concentration of 400 ppm Li in the final volume. Dilute the solution until the K concentration falls within the 50 to 125 ppm K range, if possible. Determine the K in solution by flame photometer, using the internal standard procedure.

EXPERIMENTAL RESULTS AND DISCUSSION

Analysis for K in KTPB

The proposed method for degrading soils and micaceous minerals by the removal of K with NaTPB involves the replacement of K, the precipitation of KTPB, and the removal of this KTPB from the degraded material. The amount of degradation achieved may then be estimated by determining the increase in NH_4-fixing capacity of the material (30). This method can not be used quantitatively, however, because the total adsorbed NH_4 is not readily determined. Furthermore, it cannot be used if successive degradations of the same sample are desired. On the other hand, the amount of degradation can be measured quantitatively by determining the K in the extract. Therefore, the development of an analytical method for determining K in the extract containing KTPB was essential.

At first a truly quantitative method for determining K in these extracts was needed to permit an evaluation of the methods of carrying out the degradation. That is, the selection of optimum conditions for K precipitation and of proper methods for extracting the KTPB depended on the K determinations being quite accurate. Later, in the application of the adopted degradation procedure, some sacrifice in accuracy in favor of speed and simplicity could be tolerated. The study of methods for determining K in the extract, there-

fore, was continued throughout the period of this investigation.

Because of the insolubility of KTPB in water one would anticipate that the KTPB would be extracted from the system by a non-aqueous solution. Therefore, in the development of a method for determining the extracted K, consideration must be given to the non-aqueous nature of the solution and to the presence of materials other than KTPB that this extractant may remove. Since the TPB compounds are not entirely stable, some decomposition products such as phenyl derivatives may appear during the degradation period and thus be present in the extract. The excess NaTPB and high salt concentrations used in the degradation, as well as materials the solution may dissolve from the soils or micaceous minerals, may also be present.

In the literature there are many methods for determining K through analysis for TPB, but no method for directly determining K in KTPB has been found. The methods for determining K with TPB involve the precipitation, separation, and purification of a KTPB precipitate prior to the weighing of the KTPB or the determination of the TPB combined with K. In some of these methods the decomposition of NaTPB must be restricted to negligible amounts. The success of all methods requires that any contaminant be removed by washing with KTPB-saturated water, or that it have no influence on the

determination of the TPB group. Therefore, none of these methods can be applied directly to the determination of K in the solutions of KTPB extracted from the degraded materials.

From a review of analytical methods reported in literature and a consideration of the specific character of the extract the following types of analysis were selected for study: (1) dry ashing; (2) wet ashing and acid hydrolysis; (3) decomposition of TPB by $HgCl_2$; (4) precipitation of TPB as AgTPB; (5) direct determination of K in acetone by flame photometer; and (6) ion exchange resin separation of K from TPB.

Dry ashing

One of the simplest approaches to the problem of determining K in KTPB was to heat the KTPB in a muffle to convert it to KBO_2 (metaborate), to dissolve this compound in dilute acid, and to determine the K in the aqueous solution with a flame photometer. Thus, to evaluate the application of dry ashing to the analysis of K in KTPB the following experiment was performed. Five ml. of a 1000 ppm K solution (KCl) and 2 ml. of a 4.5% NaTPB solution were added to several 50-ml. Erlenmeyer flasks and 30-ml. platinum crucibles. Contents of the flasks and crucibles were taken to dryness by evaporation on a steam plate and then ashed for 1 hour at different

temperatures in thermostatically-controlled electric muffles, in which the temperature did not fluctuate more than 40° C. After the ashed samples had cooled, the sides of the flasks were washed down with 30 ml. of 0.4 N HCl (15 ml. in the case of crucibles). The samples were digested on a steam plate for at least 1 hour before the solution was filtered, and the flask and residue were washed with hot (ca. 60° C.) water. The combined filtrate and wash were made to 100 ml. volume after the addition of LiCl. K recoveries as determined by flame photometer analyses of the filtered ash digest are listed in Table 1.

Table 1. Recovery of K from KTPB by dry ashing in Pyrex and platinum containers

Ashing temperature (° C.)	Recovery of added K (%)	
	In Pyrex	In platinum
150	97.1	94.4
185	--	94.4
200	97.2	--
225	--	98.5
250	96.4	--
280	95.5	--
330	89.8	--
400	--	99.9
430	85.2	--
460	--	99.7
480	80.8	--
520	--	99.4
530	61.8	--
580	--	98.8

From Table 1 it is seen that ashing in the Pyrex flask did not yield quantitative recovery of K. While the Pyrex flasks used did not reach red heat at temperatures below 500°, it is possible that the glass did fuse with K to a marked degree at temperatures lower than 500° C. The work by Geilmann and Gebauhr (25) indicates that decomposition of KTPB heated for 1 hour at 150° C. and 200° C. is only 0.5% and 1.0%, respectively. Thus, much of the recovery at the lower temperatures reported here was probably due to hydrolysis of unashed KTPB by the dilute HCl added after ashing.

Ashing in platinum crucibles at 400° C. gave complete recovery of K from KTPB. At 150° C. the TPB sample gave off a strong phenolic odor. However, it wasn't until the temperature exceeded 400° C. that the precipitate assumed less of a "toasted" appearance and took on more of an ash character. At about 530° C. ashing was complete; above this temperature marked loss of K was observed.

When enough platinumware is available, heating at 400° C. would be a logical method of determining K in KTPB. The large number of samples and the large volumes of extract anticipated in the degradation experiments, however, made this method impractical in the present investigation. Thus other methods were investigated to find one that was adapted to glassware.

In view of near quantitative recovery of K from KTPB at the lower temperatures in the Pyrex flasks, an attempt was

made to increase K recovery by treating the precipitate previous to muffling. It was felt that nitration of the phenyl groups and hydrolysis of the precipitate through heating with concentrated HNO_3 prior to muffling might increase the recovery of K from KTPB.

Thus, to 50-ml. flasks containing dry KTPB and NaTPB (prepared from KCl and NaTPB as before) there were added 5 ml. of concentrated HNO_3. The flasks were then heated on a steam plate. When the acid had been reduced in volume to about 1 ml., the precipitate was completely dissolved. Once the flask contents had reached dryness, they were then ashed in a muffle for 1 hour, taken up in dilute HCl, and filtered. The flasks and residues were washed with hot water, and the filtrates were then analyzed for K as before.

For the 250°, 330°, and 480° mufflings only 2 ml. of concentrated HNO_3 were used. At each of these three temperatures 20 ml. of water were added to one of the duplicate samples before the HNO_3 addition, without affecting K recovery. Results from this experiment are recorded in Table 2.

No results were obtained for the 250° C. treatment because the samples were lost by explosion. This explosion of the nitrated precipitate occurred only in the case of the samples which were held in the vicinity of 235° C. Actually, these samples underwent an initial rise in

Table 2. Recovery of K from KTPB by dry ashing the nitrated KTPB

Ashing temperature (° C.)	Recovery of added K
540	78.3
480	80.8
400	89.9
330	91.0
280	96.9
250	-- *
200	98.9
150	98.9

*Sample lost by explosion

temperature to 255°, a fall to 225°, and a rise to 235°, at which point the samples exploded "in salvo". Duplication of conditions for additional samples resulted in the same timing of the explosion. No other samples exploded during the course of the experiments.

The recovery of K by dry ashing KTPB in Pyrex containers was not increased appreciably by the prior treatment with HNO_3. Since K was not recovered quantitatively by dry ashing at high temperatures, this approach was not pursued further.

As was the case in the first experiment, high K recoveries were obtained at the low temperatures. Much of this was probably due to hydrolysis by the HNO_3 or HCl used in the experiment. Therefore, another attempt was made to maximize the recovery of K from KTPB in Pyrex containers by

treating the sample with HNO_3 or aqua regia, then heating it in a muffle at a low temperature, and finally hydrolyzing the product further with HCl, HNO_3, or aqua regia. It was anticipated that this method might release more K than would a single treatment.

To 50-ml. flasks were added 5 ml. of a 1000 ppm K solution (KCl) and 2 ml. of a 4.5% NaTPB solution. To six of these flasks were added 2 ml. of concentrated HNO_3, and to six other flasks were added 2 ml. of aqua regia (4:1 by volume of concentrated HCl to concentrated HNO_3). All flasks were taken to dryness on a steam plate and heated for 1 hour at 185° C. Duplicate pairs of flasks were then subjected to additional hydrolysis by the addition of 2 ml. of concentrated HNO_3, 2 ml. of aqua regia, or 1 ml. of concentrated HCl. Thirty ml. of water were added to one flask of each duplicate pair. Then all of the flasks were placed on a steam plate. When the concentrated HNO_3 had become reduced to about 1 ml. of volume on the steam plate, 30 ml. of water were added to all of the concentrated acid flasks. After an additional hour on the steam plate all samples were filtered and washed with hot water. The filtrate was then analyzed for K. Since there was no difference in K recovery between samples treated with the dilute acid during the second acid treatment and those treated with the concentrated

acid, results reported in Table 3 are average values for the K recovered under the two conditions.

K recovery from KTPB was not increased by treating the sample with concentrated acid after it had been heated in the muffle. Still, the K recovery was relatively good. Therefore, the question arose as to whether the method could be simplified by omitting the heat treatment.

Table 3. Recovery of K from KTPB by acid treatment before and after heating to 185° C.

Initial acid treatment	Second acid treatment	Recovery of added K (%)
HNO_3	HCl	98.8
	HNO_3	98.5
	Aqua regia	98.4
Aqua regia	HCl	97.9
	HNO_3	97.7
	Aqua regia	99.3

Wet ashing and acid hydrolysis

From observation as to the changes undergone by KTPB during acid hydrolysis as contrasted with those undergone by heating to the vicinity of 200° C., it seemed probable that acid treatment had played a greater role in the recovery of K than had heat treatment. For this reason wet ashing and acid hydrolysis were tested to determine whether such treat-

ments by themselves might recover K from KTPB as efficiently as did the more involved methods reported above. While this section dealt largely with acid oxidizing systems, it seemed well to investigate at the same time a hydrolyzing agent such as HCl.

To study hydrolysis of KTPB by HCl, 5 ml. of a 1000 ppm K solution (KCl) and 2.5 ml. of a 3% NaTPB solution were added to 125-ml. flasks. The contents of these flasks were then taken to dryness on a steam plate.

To six of these flasks were added 10 ml. of N HCl, and to four were added 3 ml. of concentrated HCl. All flasks were covered with watch glasses and digested on a steam plate for the length of time required to cause the complete disappearance of precipitate from the bottom of the flask and, at the same time, to effect a film of hydrolyzed resinous residue on the liquid surface.

In the analyses for K in the flame photometer, it is preferable that the solutions be acid-free. Therefore, to determine the advisability of removing the acid by evaporation at this point, one pair of samples hydrolyzed at each acid strength was dried on a steam plate. One hundred ml. of water were added to each flask. The samples were digested on a steam plate for 3 hours. The digests were filtered, the flasks and residue were washed with hot water (ca 60° C.), and LiCl was added to the filtrate-washes. The cooled fil-

trates were made to volume and analyzed for K. K recovery by this method was 97.2%.

To maximize the recovery of K from KTPB by HCl hydrolysis a longer digestion period was used. Following an initial 2 hours of hydrolysis with 10 ml. of N HCl, 80 ml. of water were added to two of the KTPB-NaTPB systems. Hydrolysis was then continued for 2 hours. In this case the hydrolyzate was filtered before the acid was removed by drying. The residue was digested with water on a steam plate and the K in solution was then determined. Recovery by this method was 99.1% of the added K.

To determine the necessity of digesting the sample after the initial acid digest had been diluted with water, pairs of samples digested at each acid concentration were filtered immediately after the initial digestion period. The flasks and hydrolyzed residues were washed with hot water, the filtrates were freed of acid by drying, and the K in the filtrates was determined. K recovery was 99.1% for the concentrated HCl treatment and 99.0% for the N HCl. These results indicate that the initial 2-hour digestion period was responsible for the K recovery.

In summary, the results of these experiments showed that K can be quantitatively recovered from KTPB by hydrolyzing the precipitate with HCl. The normal and concentrated HCl additions were equally effective in this regard. To insure

maximum recovery of K the hydrolyzed material should be removed by filtering before the acid is removed from the hydrolyzate.

It was anticipated that acetone extracts of KTPB from degraded soils would contain soil organic matter, which could interfere in the recovery of K from KTPB. To oxidize such organic matter at the same time that one decomposes the KTPB precipitate would seem logical, since common acid hydrolyzing agents such as HNO_3 and, more particularly, aqua regia, possess strong oxidizing properties. Therefore, hydrolyzing experiments were carried out with these acids.

For the study with HNO_3 and aqua regia 5 ml. of a 1000 ppm K solution (KCl) and 3 ml. of a 3.4% NaTPB solution were added to each of ten 125-ml. flasks. The contents of the flasks were reduced to dryness on a steam plate.

At this point 2 ml. of concentrated HNO_3 were added to three flasks, while 20 ml. of water and then 2 ml. of concentrated HNO_3 were added to three other flasks. The acids were evaporated on a steam plate to the point of complete solution of the precipitate. The solutions were each diluted with water to a volume of about 60 ml. They were then digested overnight on a steam plate, cooled, and filtered. The flasks and hydrolyzed residue were washed with hot water, and LiCl was added to the filtrate. The solutions were then brought to volume and analyzed for K. Recoveries of K with

the concentrated and dilute HNO_3 treatments were 98.4% and 98.5%, respectively.

In an attempt to abbreviate the hydrolysis period used, two of the KTPB-NaTPB samples prepared above were treated with 2 ml. of concentrated HNO_3 as above, to the point of solution of the precipitate in the acid. At this point the solution was diluted, the hydrolyzate separated from the hydrolyzed residue, and K was determined. K recovery was 98.8%, indicating complete hydrolysis of the precipitate at the point of its solution in HNO_3.

The last experiment was repeated using 2 ml. of aqua regia in place of the 2 ml. of concentrated HNO_3. The flasks were covered with watch glasses immediately after addition of the aqua regia and allowed to stand at room temperature for 30 minutes. The acid was then reduced to 0.5 ml. volume on a steam plate (the residue was not dissolved). The hydrolyzate was diluted by water and separated from the hydrolyzed residue by filtration. K recovery by this method was 98.5% of the K added.

This method of recovering K from KTPB by wet ashing with aqua regia was also used in a study of optimum conditions for precipitation and recovery of K in KCl solutions. The results of these experiments, which are reported later in this thesis, show that 99.1% to 99.7% of the added K may be recovered by this method.

These experiments with HNO_3 and aqua regia show that K can be quantitatively recovered from KTPB by these acids. The results with HCl, HNO_3, and aqua regia were equally good, but in anticipation of the need of destroying organic matter in acetone extracts of degraded soils, methods using aqua regia were adopted for further development of the degradation procedure. However, since this method is tedious and time consuming, a search for a simple rapid method was continued.

Decomposition of KTPB by $HgCl_2$

Wittig *et al.* (61) reported that KTPB reacts with $HgCl_2$ in the following manner:

$$K[B(C_6H_5)_4] + 4HgCl_2 + 3H_2O \rightarrow H_3BO_3 + 3HCl + 4C_6H_5HgCl + KCl$$

Flaschka *et al.* (20), Flaschka and Sadek (22), and Amin (2) devised quantitative procedures in which the acidity produced by the above reaction was used as an indirect measure of K. If this reaction goes to completion, one would expect that K would be released quantitatively to a state in which it could be determined by flame photometer.

To investigate the use of $HgCl_2$ in freeing K from KTPB, 5 ml. of a 1000 ppm K solution (KCl) and 3 ml. of a 3.4% NaTPB solution were added to each of 16 125-ml. flasks. To six of these flasks there were added 10 ml. of a 3.5% $HgCl_2$

solution. To four other flasks there were added 8 ml. of acetone and 10 ml. of a 3.5% $HgCl_2$ solution. According to the above equation, this addition of $HgCl_2$ (350 mg.) was 40% in excess of the amount required to react with the TPB in the 102 mg. of NaTPB present.

Following the addition of the $HgCl_2$, the aqueous systems were treated in various ways before filtration to separate the K in solution from the decomposition residue. One pair of flasks was held at room temperature for 4 hours; another pair was boiled for 30 minutes on a sand bath; and a third pair was taken to dryness on the steam plate, then digested in 25 ml. of water for 30 minutes on the steam plate. Two of the systems containing acetone were filtered; then all four were taken to near dryness on a steam plate. Recovery of K, following the filtration of all ten samples and the analysis of filtrate, fell within the narrow range of 69.6% to 70.8% K.

To determine the influence of an increase in $HgCl_2$ on the recovery of K, 5-, 10-, and 20-ml. portions of a 3.5% $HgCl_2$ solution were added to aqueous systems containing K and NaTPB in the same amounts as the previous experiment. After the samples had stood for 25 hours at room temperature, they were filtered and washed with water. Analysis of the filtrates indicated recoveries of 70.3%, 70.5%, and 69.1% K, respectively. These additions of $HgCl_2$ ranged from 70% to

280% of the stoichiometric requirement for the decomposition of the TPB present, yet there was no effect of variations in the amount of $HgCl_2$ added on the recovery of K.

As the amount of $HgCl_2$ had had no influence on the recovery of K, it was questioned whether or not the excess NaTPB was affecting the K recovery by this method. Therefore, four aqueous systems containing KTPB and NaTPB were prepared in the same manner as before, with the exception that the volume of 3.4% NaTPB solution used was doubled to 6 ml. Two of these systems received 10 ml. of 3.5% $HgCl_2$, while the other two received 20 ml. After standing for 25 hours at room temperature, the flask contents were filtered, and the filtrates were analyzed for K. Recovery was only 55.5% of the 5 mg. added in either case. These results indicate that the excess NaTPB or a decomposition product of NaTPB was responsible for the low K recovery by this method.

In these experiments it was necessary to verify that the K analyses with the flame photometer were not being affected by the presence of mercuric ions. Therefore, 0.5- and 1-gram $HgCl_2$ additions were made to 100-ml. aliquots of 50 ppm K standard solutions (KCl). No change was observed in the flame photometer readings from those obtained with comparable Hg-free standards.

To further study the reaction of $HgCl_2$ with TPB, 10 ml. of a 3.5% $HgCl_2$ solution were added to 3 ml. of a 3.4% NaTPB

solution in a 125-ml. flask. The solution was filtered after 25 hours, and 5 ml. of a 1000 ppm K solution (KCl) were added to the filtrate. This solution was then analyzed for K with the flame photometer. No K precipitation was observed when the K was added, but only 71.4% of the added K was "recovered" by the analysis.

Under the conditions studied above, K recovery from KTPB treated with $HgCl_2$ was a function of the amount of TPB added. While it appears that the formation of a visible precipitate was not the reason for the low recovery of K, the nature of the interference is unknown.

Precipitation of TPB as AgTPB

According to Rüdorff and Zannier (46), KTPB can be determined by dissolving the KTPB in a minimum of acetone and titrating it with $AgNO_3$ to an eosin end point. KBr and HOAc are added to sharpen the eosin end point. This titration is based on the fact that AgTPB is relatively insoluble in acetone, while KTPB is very soluble. Therefore, by adding $AgNO_3$ to an acetone solution of KTPB it should be possible to precipitate all of the TPB, leaving the K free to be determined with the flame photometer. When this work was being done, it was already apparent that the extraction of KTPB from degraded materials would be effected by acetone. An adaptation of this method to the determination of K in

these extracts, therefore, appeared quite desirable.

Five ml. of a 1000 ppm K solution (KCl) and 3 ml. of a 3.4% NaTPB solution were added to a 125-ml. flask. The flask contents were dried by heating on a steam plate. Then, according to an adaptation of the method of Rüdorff and Zannier, 3 ml. of acetone, 1 ml. of 0.2 N NaBr, and two drops of 0.1% eosin were added. NaBr was used rather than KBr, since the quantitative recovery of a known K addition was being determined. Titration by 0.1 N $AgNO_3$ to a pink end point (ca 6.1 ml.) followed. After titration the sample was filtered once or twice (twice if new solid material separated after the first filtration). The filtrate was taken to dryness, and the dried residue was digested with water. The filtrate then obtained by filtering this digest was analyzed for K in the flame photometer.

Whether filtration was immediately after titration or after a delay of 20 minutes, whether samples were filtered once or twice before drying of the filtrate, K recovery lay in the range of 88.5% to 92.2%.

This experiment was repeated to determine whether or not $AgNO_3$ additions beyond the eosin end point would increase the K recovery. In this experiment 0.5 ml. of a 8 N HOAC - 0.1 N NaBr solution was used instead of the 1 ml. of 0.2 N NaBr. Also, a 0.5 N $AgNO_3$ solution was used so that the acetone-water ratio would be higher. Under these conditions,

a maximum separation of K from TPB should be obtained, according to Rüdorff and Zannier (46).

The recovery of K obtained, however, was between 89.5% and 95.2%, whether the titration was stopped at the eosin end point or an excess of $AgNO_3$ ranging from 45% to 230% was used. Therefore, this method could not be used to determine K in the KTPB extracted from degraded materials.

In the method proposed for the degradation of soils and micaceous minerals it was anticipated that high concentrations of salts would be used to cause the replacement of K. An acetone-water extract of the degraded material would, therefore, contain these salts. To eliminate interference from these salts in subsequent K analysis by flame photometer, this extract would be dried, and the KTPB residue would then be leached free of water-soluble salts. Then, if the TPB could be separated from K in an aqueous system instead of in acetone, K could be determined directly, and the additional steps of removing acetone would be avoided. While there was no information in the literature on the relative solubilities of KTPB and AgTPB in water, there was a possibility that TPB could be separated from K by Ag in aqueous solutions, just as it is supposed to do in acetone.

Accordingly, 5 ml. of a 1000 ppm Li solution ($LiNO_3$) and 3 ml. of a 3.4% NaTPB solution were added to 12 50-ml. volumetric flasks. To half of the flasks (the odd-numbered

flasks) were added 5 ml. of a 1000 ppm K solution (KCl). Thus, in these flasks KTPB was formed before the addition of $AgNO_3$.

To flasks 1 through 6 of the 12 flasks there were added two drops of 0.1% eosin and 5 ml. of 2 N HOAc (to provide the proper pH for eosin color change). End points for the $AgNO_3$ titrations were observed in these flasks. To each flask was measured one of the following volumes of a 0.1 N $AgNO_3$ solution: 2.7 ml., which was less than the amount required to precipitate the 0.3 me. of NaTPB present; 4.0 ml., which was less than that equivalent to 0.3 me. of NaTPB plus 0.13 me. of KCl; and 5 to 6 ml., which was an excess. Five ml. of a 1000 ppm K solution (KCl) were then added to the even-numbered flasks. The flasks were made to volume and shaken. Their contents were filtered, and the filtrates were immediately analyzed for K.

When enough $AgNO_3$ had been added to the TPB solutions to precipitate all of the TPB before KCl was added, whether or not the $AgNO_3$ addition was sufficient to precipitate all of the subsequently added chloride, recovery of K in the filtrate by flame photometric methods was within a 70.5% to 71.4% range.

When the $AgNO_3$ added to the flasks containing KCl was equivalent to 90% of the NaTPB present, 65.4% of the added K was recovered. When more than an equivalent amount of

$AgNO_3$ was added to the flasks containing KCl, recovery of K in the HOAc-bearing solutions was 6.3%, as opposed to 0.8% recovery in the absence of HOAc.

Direct determination of K in acetone by flame photometer

Another analytical method considered was the analysis for K by passing KTPB dissolved in acetone through the flame photometer to obtain a direct measurement of the K contained therein. Such a method would be particularly desirable, since it would allow one to effect a rapid analysis of the KTPB extracted from degraded minerals.

Acetone possesses the instability of an unsaturated hydrocarbon and, as such, can be mixed with propane in a flame photometer only with extreme caution. Thus, flame characteristics of acetone-bearing aqueous solutions were studied first in the low range of acetone concentration. Since aqueous solutions containing 20% acetone by volume can dissolve about 50 ppm K as KTPB, it is possible that dilute solutions of acetone in water may dissolve enough KTPB to make feasible the analysis of K in KTPB.

In a preliminary observation, aqueous solutions containing 0, 5, 10, and 15% acetone by volume as well as 50 mg. of K per l. were analyzed for apparent K contents with a Perkin-Elmer flame photometer. Propane gas was used as fuel, and solutions of KCl in water were used as standards. The

internal standard method was used. Apparent concentrations of K determined in the 0%, 5%, 10%, and 15% acetone solutions were 50.0, 52.5, 58.0, and 78.0 mg. of K per l., respectively.

Since acetone modified the K reading to such a marked degree, the next step was to select Li and K concentrations at which the presence of acetone would least affect the K determination. The following water-acetone solutions were prepared: 20% (by volume) acetone solutions containing 800 mg. of Li per l. and 50 or 250 mg. of K per l.; and 20% acetone solutions containing 4000 mg. of Li per l. and 250 or 1000 mg. of K per l. The K in these acetone-water solutions was again determined with a Perkin-Elmer flame photometer, using propane gas and employing standards of KCl in water. Both direct intensity and internal standard methods were used in these determinations. The errors observed in K determinations with the acetone-water solutions are given in Table 4.

Table 4. Error in K determinations in acetone-water solutions

Li in solution (mg./l.)	K in solution (mg./l.)	Error in K determination (%)	
		By direct intensity method	By internal standard method
800	50	86.0	54.2
800	250	22.6	79.6
800	250	31.8*	--
4000	250	35.8	38.0
4000	1000	33.2	72.5

*This value was determined at a later date.

It was apparent from these results that accurate determinations of K in acetone-water solutions could not be made in this manner. Determinations made 1 month apart on the same solutions showed marked variability. In all of these determinations with solutions containing acetone, the meter stability was very poor. Thus, a direct flame photometer analysis of K in the acetone extracts of degraded materials does not appear feasible.

Ion exchange resin separation of K from TPB

Flaschka and Sadek (22) ran acetone-water solutions of KTPB through H-saturated cation exchange resin and determined the KTPB indirectly by titrating the displaced H in the effluent. Amin (2) modified this method by determining the total acidity in the effluent after TPB contained therein had reacted with $HgCl_2$. In both cases, however, a cation exchange resin was used to separate K from TPB. Flaschka and Sadek stated that Hegemann and Pfab (32) had separated metals quantitatively from TPB salts in this manner. However, such a method for K was not found in the article cited. Nevertheless, this latter approach offered one of the best possibilities for a simple and rapid method of determining K in the acetone-water extracts of degraded materials.

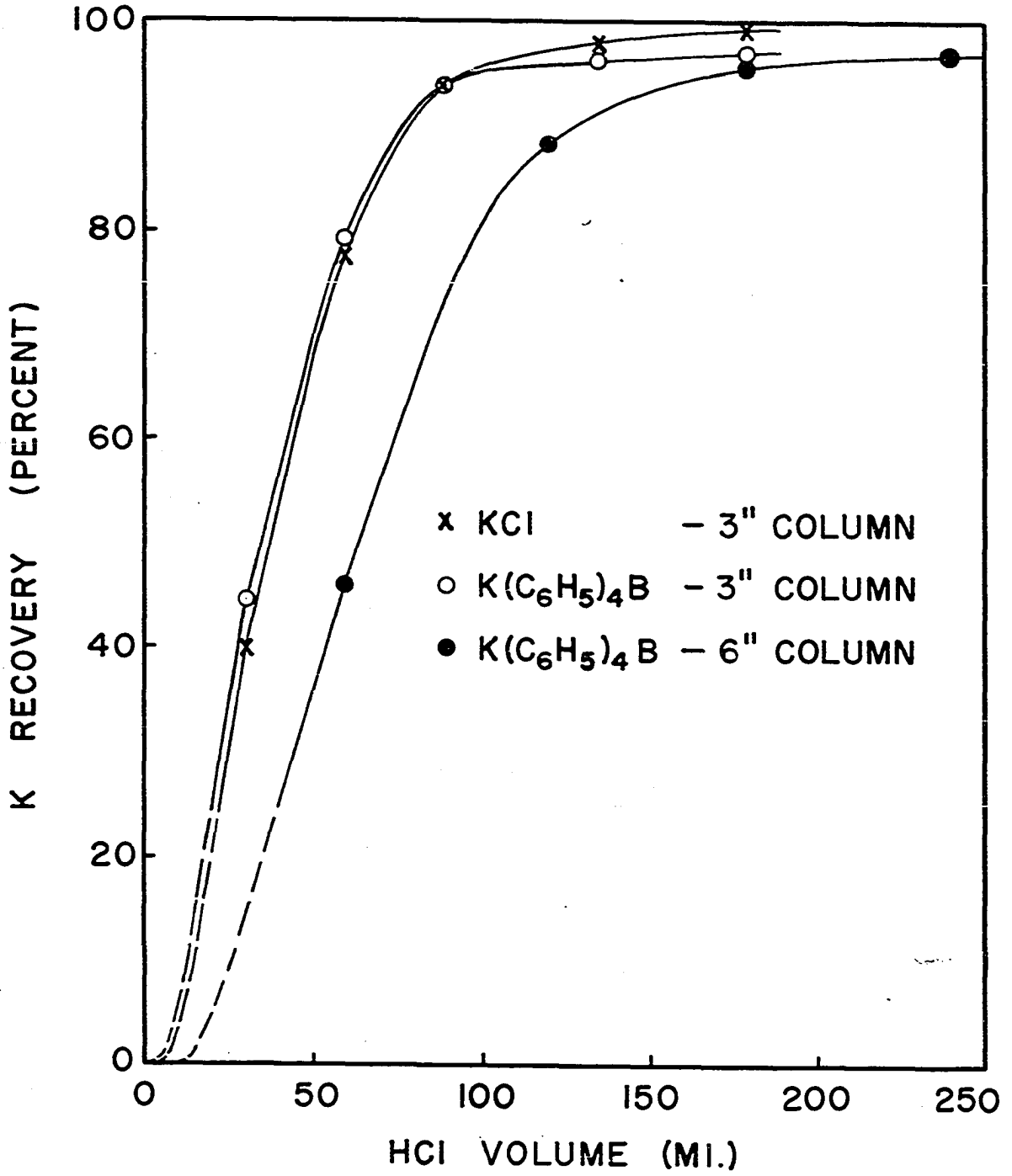
To investigate this procedure H-IR-120 columns 0.5 inch in diameter, 3 inches or 6 inches in length, and possessing

exchange capacities of 22 or 44 me., were prepared. KTPB-NaTPB solutions were prepared by mixing 5 ml. of a 1000 ppm K solution (0.13 me. K as KCl), 3 ml. of a 3.4% NaTPB solution (0.30 me.) and 8 ml. of acetone in 50-ml. flasks. Comparable KCl solutions were made by adding 5 ml. of a 1000 ppm K solution (KCl) to flasks containing 3 ml. of water and 8 ml. of acetone.

Each solution prepared above was passed through a H-IR-120 column at the rate of 1 to 4 ml. per minute. Each flask and resin column was washed twice with 5-ml. portions of a 1:1 acetone-water solution and once with 10 ml. of water. The columns were leached with 30, 45, or 60 ml. increments of 2 N HCl. After each increment of acid the columns were leached with 15 or 30 ml. of water, and the combined acid increments plus water washes were taken to dryness on an electric hot plate. Beakers containing the dry residue were washed down with about 30 ml. of water and digested at low heat for 30 minutes. K in the water was then determined by flame photometer. The cumulative recovery of K from the resin with HCl is graphed in Figure 1.

There was essentially complete recovery of the K added to the resin as KCl. Therefore, the presence of acetone did not interfere with the exchange of K for H on the resin. Only 97% of the K added as KTPB was recovered, however, even though the resin was leached with 16 symmetry concentrations

Figure 1. K recovery by HCl from cation exchange resin columns that had been leached with acetone-water solutions containing KTPB or KCl


100
80
60
40
20
0
K RECOVERY (PERCENT)
0
50
100
150
200
250
HCl VOLUME (Ml.)
x KCl – 3" COLUMN
○ K(C6H5)4B – 3" COLUMN
● K(C6H5)4B – 6" COLUMN

of HCl. The recovery of K from KTPB was not increased by passing the acetone-water solution of KTPB through a longer resin column. The reason for this low recovery is still unknown.

The cation exchange method of recovering K from KTPB is rapid and is probably sufficiently quantitative for most purposes. More study of the method is needed, however, before it can be adapted to routine degradation experiments. One definite limitation to this method is the limited amount of salt that can be present in the extract. K will be retained by the resin only if the exchange capacity of the resin sample exceeds by large measure the total cations in the solution. This difficulty may be overcome, of course, by prior removal of the salts.

Anion exchange resins have also been tested to a limited extent for use in the separation of K from TPB. Flaschka and Sadek (22) noted that "variable degrees of exchange resulted" when acetone solutions of KTPB were passed through strong anion exchangers. Because of the inexact nature of their statement as to the reason for their rejection of the anion exchange resin as a means for K recovery from KTPB, and because it was known that Amberlite IRA-410 is able to retain weakly ionized anions, it was thought that K might be quantitatively separated from the TPB by passing an acetone solution of KTPB through IRA-410. Thus, columns of IRA-410,

6 inches long and 0.5 inch in diameter, were prepared and washed with 400 ml. of N NaOH to saturate the resin with OH ions. They were then washed with water until their eluate had a neutral pH.

To 125-ml. flasks were added 5 ml. of a 1000 ppm K solution (KCl) and 3 ml. of a 3% NaTPB solution. To these solutions were added 6 or 18 ml. of acetone. Comparable KCl solutions were prepared by diluting 5 ml. aliquots of a 1000 ppm K solution (KCl) to 8 ml. with water, to 14 ml. with water and 6 ml. of acetone, and to 26 ml. with water and 18 ml. of acetone. These solutions were passed through the exchange columns at rates varying from 1 to 4 ml. per minute. The columns were rinsed twice with 5-ml. portions of 1:1 acetone-water and then with water alone. The added K was quantitatively recovered in the combined eluate-wash from all KCl solutions, while no more than 6% of the K was recovered from solutions that contained TPB. Thus, it was seen that this method of using an anion exchange resin did not offer promise.

Of the various methods studied above for the recovery of K from KTPB the dry ashing at 400° C. in platinum ware, the acid hydrolysis (as by aqua regia), and the recovery by cation exchange resin appear to be the most satisfactory. The first method has the disadvantage of requiring special ware; the second method is tedious; the third method gives

slightly lower K recovery than the other two methods and requires the use of low salt concentrations.

Precipitation and Recovery of K from KCl

Once a method of analysis for K in KTPB had been selected, it was necessary to show that KTPB could be precipitated, filtered, and then redissolved under the environmental conditions anticipated in the proposed degradation experiments.

The literature contains numerous references relating to the precipitation of KTPB (11, 26, 36). It has been observed that this precipitation and the stability of the TPB compounds are affected by temperature and pH. There is, however, no agreement as to the optimum conditions to use (53, 54). At the same time, certain environmental conditions are needed for the replacement of fixed or lattice K in the degradation experiments. For instance, the replacement of K can be increased by increasing the temperature, by lowering the pH, and by increasing the concentration of hydrated replacing cations. Therefore, it was necessary to determine whether K could be precipitated and recovered under conditions that were desirable for K replacement.

Precipitation and recovery of K added to Morgan's solution

K replacement is generally increased by a decrease in the pH of the extracting solution. However, some destruction of the mineral crystal lattice may occur when the pH is allowed to reach too low a point. A moderately acid, buffered extracting solution such as Morgan's solution (pH 4.8) would appear to be a desirable extractant to use in degradation experiments. Therefore, the precipitation and recovery of K added to Morgan's solution was determined.

The form of the KTPB precipitate, and thus its retention on a filter, is affected by the pH of the solution in which it is precipitated. Thus, it was necessary to select a filter that would retain the precipitate formed under the conditions of these experiments. Spier (50) recommended several filters, including "Glas filter G-4", for the separation of KTPB from its precipitating medium. Cluley (15) and Sporek and Williams (51) used No. 4 porosity sintered glass crucibles. Therefore, Jena No. 5 porosity sintered glass Buchners, which happened to be available at the time, were used here in a preliminary experiment.

To a pair of 25-ml. flasks were added 5 ml. of a 1000 ppm K solution (KCl), 2 ml. of water, and 10 ml. of a 2 N Morgan's solution (N NaOAc - N HOAc). Three ml. of 3.4% NaTPB were then added dropwise, with swirling of the flasks.

Contents of the flasks were filtered on the Jena No. 5 porosity sintered glass Buchner funnels. The precipitates on the funnels were washed with six to eight drops of water, then five times with 5 ml. of KTPB-saturated water, and finally with six to eight drops of water.

The receiving flasks were exchanged for clean ones, and the precipitates were washed through the sintered glass filters with about 40 ml. of 1:1 acetone-water solution. The dissolved precipitates were transferred to 250-ml. beakers and freed of acetone by evaporating to dryness on a steam plate. These precipitates were then hydrolyzed with aqua regia, and the K in the hydrolyzate was determined.

Recovery of K following this procedure averaged 99.7%. These results demonstrate that K can be quantitatively precipitated and recovered from Na solutions at pH 4.8.

A similar experiment was then carried out using the more readily available Pyrex sintered glass Buchner funnels and the more detailed procedure anticipated in the degradation experiments.

To three 125-ml. flasks were added in order: 5 ml. of a 1000 ppm K solution (KCl), 25 ml. of a 2 N Morgan's solution, 5 ml. of 3.4% NaTPB, and 15 ml. of water. The samples were shaken on a wrist shaker for 10 minutes, heated in an oven at 70° C. for 9 hours, shaken again for 10 minutes, and cooled. In a simulated separation of KTPB from degraded

mineral, 50 ml. of acetone were added to the flasks to dissolve the KTPB. The flask contents were mixed by swirling and filtered through Whatman No. 42 filter paper on porcelain Buchner funnels. The flasks and filter paper were washed with 5 ml. of a 1:1 acetone-N Morgan's solution and then with water. The filtrates were transferred to beakers and evaporated to dryness on a steam plate. About 50 ml. of water were then added to the beakers, after which the beaker contents were allowed to digest on the steam plate, with occasional agitation by stirring rod. The beaker contents were filtered through 60-ml. medium porosity Pyrex sintered glass Buchner funnels. The beakers and funnels were washed twice with 2 to 3 ml. of water. The precipitate was then washed through the glass Buchners into clean filter flasks with about 50 ml. of a 1:1 acetone-water solution. The acetone was removed by evaporating the solution to dryness on a steam plate. Hydrolysis of the precipitate by aqua regia and analysis of the hydrolyzate for K followed.

The recovery of K in this experiment was 99.1%. Therefore, the precipitation of K at pH 4.8, in the presence of moderate Na concentrations, was satisfactory. The precipitate dissolved readily in the acetone-water solution. In this solution it passed through both the filter paper and the sintered glass. The KTPB was quantitatively retained by the medium porosity Pyrex sintered glass filters when the aqueous

systems were filtered.

Stability of KTPB and NaTPB

Barshad (8) has shown that the replacement of strongly adsorbed K in soils, biotite, and vermiculite is increased by increasing the amount of heat applied and the amount of time for reaction. Therefore, soils and micaceous minerals should be boiled in an extracting solution for prolonged periods for maximum degradation. The stability of NaTPB and KTPB under these conditions is, however, questionable. Geilmann and Gebauhr (25) observed 0.25% to 0.50% loss in weight when an alkali TPB precipitate was dried at 150° for only an hour. Even at room temperature neutral NaTPB solutions became cloudy. For this reason NaTPB solutions are commonly cleared of decomposition products by the use of aluminum hydroxide before they are used. After only 48 hours of standing the decomposition of a 3.4% NaTPB solution can be observed from the settling out of decomposition products. After 320 ml. of a 3.4% NaTPB solution had stood for 3 weeks at room temperature (22-26° C.) a filtration of the solution recovered 0.11 grams of material, largely insoluble in water, which had settled from the solution. This amount represents 1.0% of the weight of NaTPB present in solution.

The stability of these compounds is also affected by the pH of the solution (27). Therefore, it was necessary to

determine whether or not the elevated temperatures needed for K replacement would interfere with the quantitative recovery of K from the particular extracting solutions that might be used in the degradation experiments.

Two preliminary experiments were carried out first to evaluate the seriousness of this problem. In one of these experiments 20 ml. of a N Morgan's solution containing 102 mg. of NaTPB were boiled for 45 minutes. By the end of this time the solution volume had been reduced to 5 ml. Water was added to return the solution to its original volume, the solution was cooled for 25 minutes, and 5 ml. of a 1000 ppm K solution (KCl) were added to the faintly cloudy solution. There resulted only a slight increase in cloudiness. A subsequent addition of one drop of a fresh 3.2% NaTPB solution increased the cloudiness markedly. Apparently, most of the NaTPB present originally was destroyed by boiling and concentrating the solution.

In the other preliminary experiment K was added to a two-fold excess of NaTPB before the solution was heated at 70° C. for 9 hours, and to a four-fold excess of NaTPB after the system had been heated at 70° C. for 9 hours. The solutions used in this experiment contained no extracting salt. A determination of the K precipitated under these conditions showed recovery of 99.2% and 98.0%, respectively. In the absence of high salt concentrations the NaTPB and KTPB

were apparently quite stable at 70° C. for 9 hours. The results of these preliminary experiments indicated that serious error could arise because of the instability of TPB compounds, but that it might be avoided by the proper selection of conditions for the degradation experiment.

In order to determine these optimum degradation conditions, further studies were made of the decomposition of TPB compounds at different temperatures, for varying periods of time, and in the presence of the various salts selected for use in degradation experiments. K was added to salt solutions containing NaTPB before or after the various heat treatments. Thus, the heat influenced K recovery in one case by affecting both the precipitate and excess precipitant; in the other case, it caused decomposition of the precipitant only.

In this experiment either 2.5 or 10 ml. of a 3.4% NaTPB solution and 35 ml. of NaOAc, NaCl, or Morgan's solution were added to 125-ml. flasks, 5 ml. of a 1000 ppm K solution (KCl) were then added to half of the flasks, and all flasks were diluted to 50 ml. by the addition of water. The final salt concentration in these flasks was 4 N, 1 N, and 1 N for the NaOAc, NaCl, and Morgan's solution, respectively. The pH of these solutions was 4.8 in the case of the Morgan's solution and about 7 for the others.

Each sample was then subjected to one of the following treatments: standing at room temperature (27-32° C.) for 9 hours; heating at 70° C. in an oven for 9 hours; or auto-

claving at 122° C. and 16 pounds pressure for 1 hour. The K-devoid samples were cooled to room temperature, and to each were added 5 ml. of a 1000 ppm K solution (KCl). All flasks were then swirled and allowed to stand for 30 minutes.

At this point the flask contents were filtered through Pyrex medium porosity sintered glass Buchner funnels. The flasks and funnels were washed three times with 0.5 ml. of water. Filtrates from the incubated flasks containing NaCl and Morgan's solutions, from the autoclaved flasks containing NaOAc, and from two of the autoclaved flasks containing NaCl were diluted, after adding LiCl, until the Na concentration was less than 0.5 N and were then analyzed for K in the flame photometer.

All precipitates were recovered by washing the reaction flasks and the Buchner funnels with acetone, followed by water. The precipitates were dried on a steam plate and hydrolyzed by aqua regia. Their filtered hydrolyzates, once freed of acid by drying, were analyzed for K.

In Table 5 are recorded the percentages of the added K found in the filtrates, in the case of treatments for which the filtrates were analyzed. In cases where the filtrates were not analyzed, the percentages of the added K not recovered in the precipitate are given.

A similar experiment was performed to evaluate the use

Table 5. Effect of temperature, salt, and time of reaction on the amount of added K remaining in solution following precipitation by NaTPB

Duration and temperature of treatment	Timing of K addition (before or after heat)	Volume of 3.4% NaTPB (ml.)	Added K in solution (%)*			
			No salt	NaOAc	NaCl	Morgan's
9 hr. at 27-32° C.	before	2.5	--	0.9	3.0	1.4
	before	10.0	--	--	0.0	0.0
9 hr. at 70° C.	before	2.5	--	0.0	2.6	0.0
	before	10.0	--	--	0.0	1.8
	after	2.5	--	0.8	35.6	8.6
	after	10.0	--	--	0.0	0.1
1 hr. at 122° C. (autoclave)	before	2.5	--	36.8	25.4	95.0
	before	10.0	--	45.7	1.3	98.4
	after	2.5	--	66.5	21.2	98.1
	after	10.0	--	45.7	1.8	97.0
1 hr. at boiling point	before	5.0	5.5	26.8	4.3	--
	before	10.0	--	--	1.7	96.6
	after	5.0	3.6	76.9	4.0	--
	after	10.0	--	--	2.0	--
9 hr. at boiling point	before	5.0	4.4	49.4	4.6	--
	before	10.0	--	--	4.1	--
	after	5.0	5.5	91.2	24.0	--
120 hr. at boiling point	before	5.0	--	100.0	--	--
	after	5.0	--	100.0	--	--

*Less than half of these treatments were duplicated.

of boiling temperatures under conditions in which the solution volume was not allowed to decrease. Solutions of NaTPB, KCl, and different salts were prepared as before, with the one exception that 5 ml. of 3.4% NaTPB were used instead of 2.5

ml. as the low NaTPB treatment. The solutions were boiled for varying lengths of time in flasks fitted with reflux condensers. K as KCl was added before or after the heat treatment, as in the previous experiments. The solutions and precipitates were separated after the refluxing and the K addition, and the K in solution was determined in each as before. The percentages of the added K remaining in solution under these conditions are shown in Table 5.

The advantage of using NaTPB in the degradation experiments is to maintain a low level of soluble and exchangeable K. These experiments with added soluble K, however, show that this may not be accomplished in many cases. Thus, the instability of the TPB compounds at elevated temperatures could seriously impair the efficiency of its use in degradation experiments.

It is evident that less K remained in solution when the larger levels of NaTPB were added, when the solution was at pH 7, and when the salt concentration was only 1 N. The NaTPB rates of 2.5, 5, and 10 ml. represent precipitant excesses of 92%, 285%, and 670% over the amount equivalent to the 5 mg. of K added. In view of the high cost of NaTPB (about $50 per 100 grams) it would not be practical to use excessive amounts of NaTPB to reduce the errors resulting from reagent instability. In the degradation experiments, however, where it is expected that a large amount of K will

be precipitated, the concentration of excess NaTPB in the initial extracting solution may even exceed these levels (i.e. it may exceed 8.7 ml. of a 3.4% solution or 296 mg. NaTPB per 50 ml.).

In general it appears that the NaTPB is less stable than KTPB. That is, more K remained in solution, when the conditions were unfavorable, if the K was added after the heat treatment. Therefore, in a prolonged degradation experiment, frequent moderate additions of NaTPB may be required.

If boiling temperatures must be used, a N NaCl salt solution should be used instead of Morgan's solution. The use of 70° C., however, appears more desirable than does the use of boiling temperatures. At this temperature there was no ill effect from a lower pH (pH 4.8) or a higher salt concentration (4 N).

Influence of other cations on the precipitation and recovery of K

The replacement of K from interlayer positions in the micaceous minerals must be accomplished with cations that will cause the lattice to expand. Na and Ca are of particular interest in this regard. Since the rate of K replacement depends upon the concentration of replacing cations, information concerning the effect of large concentrations of Na and Ca on the precipitation and recovery of K was needed.

In a previously reported K recovery experiment K was

quantitatively precipitated and recovered from a pH 4.8 solution containing 1.1% Na. From Table 5 one observes that, following precipitation of K in a neutral 4 N NaOAc solution and subsequent heating of the precipitate at 70° C. for 9 hours, 98.9% K recovery was achieved. Thus, it is apparent that K can be quantitatively recovered as KTPB from solutions containing high concentrations of Na (9.2% Na in this case).

Proof of the separation of K from solutions containing large concentrations of Ca has also been obtained. Two 50-ml. solutions containing 1.4 g. of Ca were prepared from $CaCl_2$ that was found to be K-free. Five ml. of a 1000 ppm K solution (KCl) and one drop of concentrated HCl were added to each solution. Then, 4 ml. of a 3.4% NaTPB solution were pipetted dropwise into the stirred solution. After 15 minutes of standing, the KTPB was separated by filtration, washed, and hydrolyzed. Recovery of K from the precipitate hydrolyzate amounted to 99.6% of the added K. Thus it was shown that K can be quantitatively recovered from a 2.8% Ca solution by precipitation as KTPB.

It had been anticipated that, in addition to the replacing cations such as Na and Ca, NH_4 may be used at considerable concentrations in degradation work. NH_4 ions contract the lattice of some expanded micaceous mineral in a manner similar to K. While NH_4 can not be used to replace fixed or lattice K it can be used to compete with the K in solution

for fixable exchange sites. Thus it was assumed that NH_4 could be used to block the return of K to exchange positions on degraded minerals when the KTPB formed in degradation is dissolved by the extracting vehicle, acetone. Before NH_4 could be used, however, it was necessary to determine whether or not K could be quantitatively determined with the NaTPB in the presence of NH_4, since NH_4 is also precipitated by NaTPB in water.

An experiment was designed to decide whether the pH could be increased to such a point that there would no longer be NH_4 ions competing for NaTPB, without exceeding a reasonable pH level for degradation. To this end 5 ml. of 0.2 N NH_4OH were added to each of eight 125-ml. flasks. Through the addition of dilute HOAc one pair of solutions was adjusted to each of the following pH levels: 5, 7, 9, 11. All solutions were then made to 10 ml. volume with water. To each flask were added 5 ml. of a 1000 ppm K solution and 5 ml. of 3.4% NaTPB. The resulting precipitates were separated from their respective solutions by filtration, and the solutions were analyzed for K. At the pH levels 5, 7, 9, and 11 the K precipitated amounted to 53.7%, 54.3%, 60.2%, and 99.7%, respectively, of the added K.

In this experiment each flask had contained 1.0 me. of NH4, 0.13 me. of K, and 0.5 me. of TPB. This amount of TPB was only 44% of that required to precipitate both the K and

NH_4 in solution. Whereas KTPB exhibited lower solubility than NH_4TPB at all pH readings and the ratio of KTPB solubility to NH_4TPB decreased with increased pH, quantitative precipitation of K under these conditions of limited NaTPB supply was not obtained until pH 11, at which point NH_4 ion, as such, had probably ceased to exist in the solution. While Rüdorff and Zannier (46) had indicated the advisability of use of formaldehyde at a pH near 14 for the separation of K from NH_4 solution, it was shown here that the separation of K from solution can be effected at pH 11.

Solubility of KTPB in acetone-water solutions

Once the K has been precipitated as KTPB in the degradation experiments, it is then necessary to separate the KTPB from the degraded material. This may be done by dissolving the KTPB in a solvent and filtering the resulting solution from the solid residue. In previous experiments the use of a 1:1 acetone-water solution as a solvent for small amounts of KTPB has proven satisfactory. More information about the solubility of KTPB in acetone-water solutions was needed, however, so that the volume of solution and the concentration of acetone to be used for the removal of larger amounts of KTPB could be predicted.

To obtain this information KTPB was prepared by mixing 10 ml. of a 1000 ppm K solution (KCl), 5 ml. of a 3% NaTPB

solution, and one drop of concentrated HCl. After 30 minutes standing the precipitate was decanted into a conical filter paper and washed with 5 ml. of KTPB-saturated water. When larger amounts of KTPB were needed, larger amounts of these reagents in the same proportions were used.

Acetone-water solutions were prepared by mixing water and acetone in definite ratios by volume. The acetone concentration is expressed as per cent by volume of the combined acetone and water volumes used. Thus, a 50% acetone solution refers to a solution prepared by mixing equal volumes of acetone and water without regard to the final volume of the mixture.

KTPB samples prepared as described above were air dried on the filter paper, pulverized by rolling the paper cone, and then added to acetone-water solutions that contained from 0% to 44% acetone. Larger air-dried samples of KTPB were first ground in a mortar and then added to solutions that contained 50% to 100% acetone. In each case 20 ml. of solution were used and enough KTPB was added to provide an excess.

In a preliminary determination only 25%, 33%, and 40% acetone solutions were used. The flasks were stoppered and swirled at frequent intervals for the first 2 hours and last 4 hours of a 16-hour equilibration period. At the end of this period a small amount of the water-acetone solution from each flask was used to saturate a conical filter paper.

Immediately thereafter 15 ml. of the solution were filtered while the funnel containing the paper was covered with a watch glass to prevent evaporation losses. The K in the filtrate was determined by the aqua regia hydrolysis procedure.

In a second experiment the above procedure for small KTPB samples was repeated at acetone concentrations of 16%, 32%, 38%, and 44%, with two minor modifications. The KTPB was pulverized to a more consistently fine powder in this second run, and the time of solution (duration of contact between solution and KTPB) was increased from 16 hours to 48 hours.

In this second experiment acetone-water solutions containing 50%, 60%, 80%, and 100% acetone were included. These solutions were equilibrated by standing at room temperature, with occasional swirling, over a period of 48 hours. Aliquots from these solutions were pipetted directly into tared beakers, evaporated at very low heat (to prevent decomposition), and weighed to determine the weight of KTPB dissolved. The temperature of solution at which the solutions were pipetted from the flasks for analysis was 28° C. for this second experiment and 29° C. for the first experiment. During equilibration of the solutions the temperature had varied between 24° and 32° C. in each case.

The results of the two experiments are presented in Table 6 and Figure 2. It can be seen that the solubility of

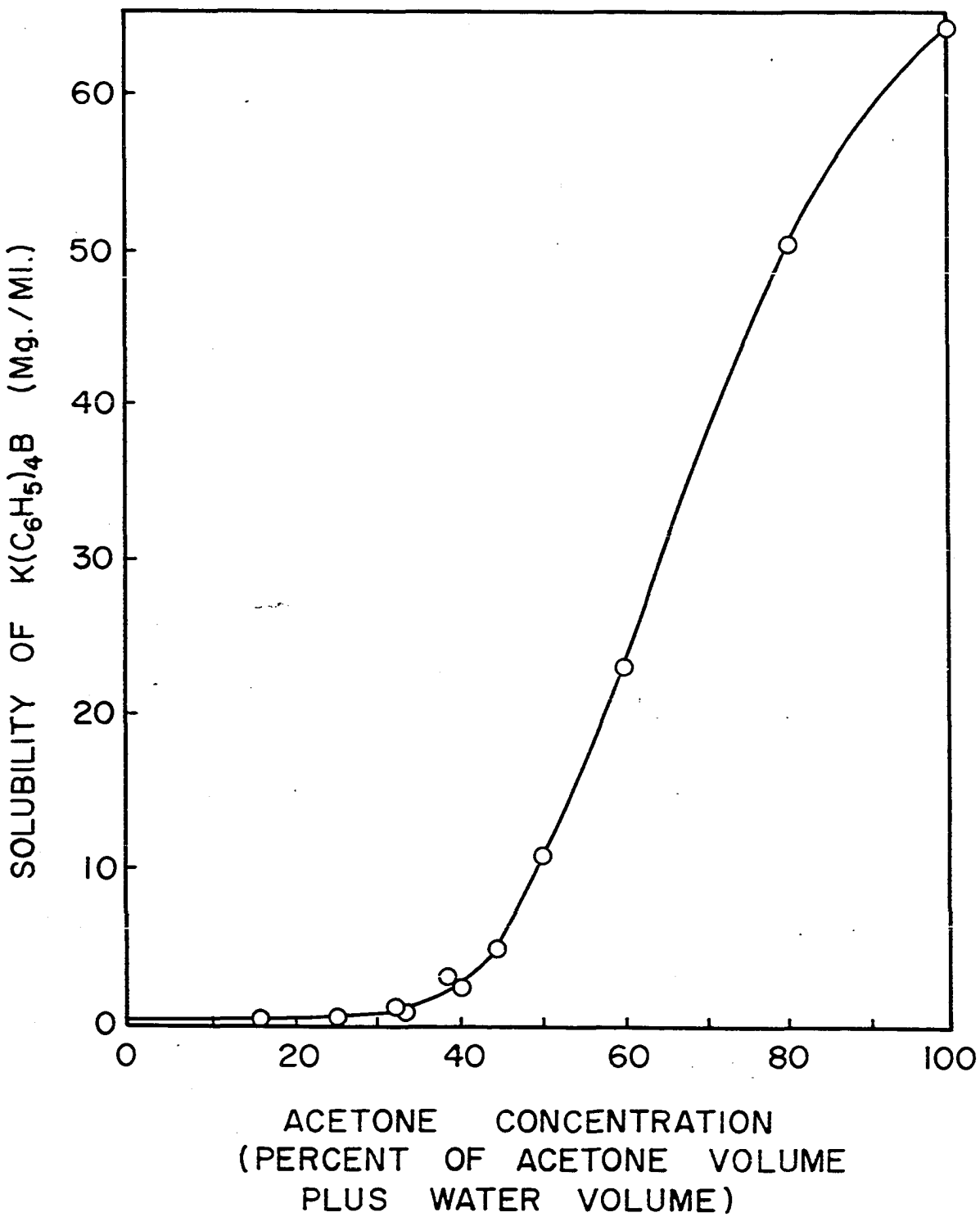
Table 6. Solubility of KTPB in solutions containing acetone and water, as a function of the acetone concentration in the solution

Acetone concentration (% by volume)*	KTPB dissolved (mg./ml.) According to Geilmann & Gebauhr (25)	Expt. 1	Expt. 2
0	.053		
16			.38
25		.58	
32			1.18
33		1.05	
38			2.92
40		2.46	
44			4.9
50			11.6
60			23.1
80			50.7
100			64.2

*Per cent by volume based on the combined volume of water and acetone used.

KTPB in acetone-water solutions increases sharply as the acetone-concentration increases from 33% to 66%. For the solution of 5 mg. of K as KTPB (45.8 mg. KTPB) 4.1 ml. of a 66% acetone solution or 35 ml. of a 33% acetone solution would be needed. That is, eight times as much solution and four times as much acetone would be needed if a 33% solution is substituted for a 66% solution in the dissolving of this amount of KTPB. This emphasizes the need for the use of high acetone-to-water ratios in the solution of KTPB, even

Figure 2. Solubility of $K(C_6H_5)_4B$ in solutions containing acetone and water, as a function of the acetone concentration


SOLUBILITY OF $K(C_6H_5)_4B$ (Mg./Ml.)
0
10
20
30
40
50
60
0
20
40
60
80
100
ACETONE CONCENTRATION
(PERCENT OF ACETONE VOLUME
PLUS WATER VOLUME)

when the amount of KTPB involved is no more than that used in these preliminary recovery experiments.

In actual degradation experiments the time of contact between degraded mineral and dissolved KTPB should be kept at a minimum to minimize the adsorption of dissolved K by the mineral. For this reason the time available for the solution of KTPB in acetone-water may be restricted to a few minutes. The amount of KTPB dissolved in this brief period of time would be less than the amount predicted from Figure 2. Therefore, to assume complete solution of the KTPB in the degraded systems, at least two or three times the acetone requirement predicted from Figure 2 has been used to remove KTPB.

Separation of KTPB from Cation Exchangers

Separation with acetone-water solutions

It was anticipated that the KTPB precipitated in the degradation of micaceous minerals would be separated from the degraded product by dissolving the KTPB in an acetone-water solution. Therefore, this method was evaluated by studying the precipitation and separation of KTPB from cation exchange materials. Amberlite IR-120 was used in many of these experiments, because there was no naturally occurring K in this material. In other experiments vermiculite was used, since, in addition to being a cation exchange material, it has a

strong affinity for K in that it fixes K under moist conditions.

Difficulty in separating KTPB from IR-120 was encountered early in this work. In one experiment 3.75 gm. of (K,Na)-IR-120 (containing 16 me. Na and 0.13 me. K) were added to flasks along with 90 mg. of NaTPB, 15 ml. of water, and enough HCl to adjust the pH to either 2.0, 6.3, or 9.2. After standing for 24 hours at room temperature, these systems were filtered and the filtrates were discarded. The flasks and the resin on the filters were washed eight times with 10-ml. portions of acetone, and then with a few ml. of water. The K in the acetone extract was determined by hydrolysis with aqua regia, following evaporation of the acetone.

A considerable amount of KTPB precipitate was observed in these resin systems when they were prepared and incubated. Thus, it was evident that exchangeable K on the resin was replaced and precipitated by the NaTPB treatment. The recovery of K in the acetone extract, however, did not exceed 54%, regardless of the pH at the time of precipitation. Since a quantitative recovery of added K was not obtained, either the K precipitation as KTPB was not quantitative, or the KTPB formed was not completely removed by acetone leaching.

It had been anticipated that K in a solution of KTPB in acetone may be retained by an exchange material. Rüdorff

and Zannier (46) have established the fact that KTPB dissolved in acetone behaves as an ionized compound. Thus, the TPB from KTPB dissolved in acetone reacts with Ag in $AgNO_3$ to form insoluble AgTPB. In a similar demonstration of the ionic nature of KTPB in acetone Flaschka and Sadek (22) retained K from an acetone-KTPB solution on a H-saturated exchange resin column and determined the K indirectly by measuring the H displaced by K. Since HTPB is a weak acid (61, 62), however, there was a possibility that the KTPB in acetone was a weakly ionized salt, and that as such it might be quantitatively removed by an acetone extraction.

Another experiment was carried out with exchange materials and KTPB alone to determine whether some of the K was not recovered in the last experiment because it was adsorbed by the exchange material. In this case 5.55 mg. of K as KTPB were added to flasks containing 3.0 gm. of Na-IR-120 or 0.5 mg. of South Carolina vermiculite. These systems were allowed to stand in 15 ml. of water for 2 hours, after which the water was analyzed for K. From the IR-120 system 0.017 mg. of K was recovered in the water, while from the vermiculite system 0.054 mg. of K was recovered. Fifteen ml. of acetone were added to each system. After 4 minutes of intermittent swirling the acetone solution was filtered from the exchange material and the latter was washed four times with 2 to 3 ml. of acetone. The acetone extract was then

dried, hydrolyzed by aqua regia, and analyzed for K.

Only 0.106 mg. of K (1.9% of that added) was recovered from the resin, while 4.57 mg. of K (82.4%) was recovered from the vermiculite. It is evident that the low recovery of K from resin observed in the first experiment was due to a loss of K to the exchange material when the KTPB was dissolved. The amount of loss to micaceous minerals, however, may not be as great as might be anticipated from the resin experiments. It is true that the vermiculite contained some K other than the KTPB added, and that this may have influenced the K recovery obtained. However, the relative loss of dissolved K to these cation exchangers is probably associated more with the difference in exchange capacities of the samples used. The 0.5 gm. of vermiculite had an exchange capacity of 0.24 me. in contrast to 13 me. in the case of the 3 gm. of resin. That is, more K was lost from solution as the number of exchange positions was increased.

It should be emphasized that no salts were added to the KTPB-exchange material systems studied above. Thus, the K ions experienced little competition for the exchange sites. That is, the conditions favored the loss of K from the acetone solution. Nevertheless, the low K recovery observed in these experiments demonstrated the necessity for selection of methods for maximizing the separation of KTPB from cation exchange materials.

Separation by sieving

One method of avoiding the low recovery of K arising from the ionization of KTPB in acetone would involve the removal of the KTPB without dissolving it. Therefore, an attempt was made to separate the KTPB from exchange materials by sieving.

Samples of Na-IR-120 and South Carolina vermiculite were sieved to remove all particles that would pass through a 32-mesh screen. To 3 gm. of Na-IR-120 or 0.5 gm. of vermiculite so screened were added known quantities of KTPB precipitate (about 60 mg.). These systems were then placed on a 60-mesh screen and the KTPB was washed through the screen with water or cyclohexane. Since KTPB is slightly soluble in water (53 mg. per l.), a continued dissolution of KTPB in water and, consequently, some loss of K to the exchange materials were anticipated. For this reason the non-polar liquid cyclohexane was included for comparative purposes.

In this experiment four pairs of samples were sieved. KTPB-resin systems from two pairs of flasks were poured onto the sieves and allowed to drain for two minutes. In one treatment the flasks and KTPB-resin were washed with 50 ml. of water applied as a fine stream, while in another treatment 50 ml. of cyclohexane were used. All four systems were then washed with an additional 80 ml. of the same vehicle. The KTPB recovered here was kept separate from that recovered in the 50-ml. wash.

The two remaining pairs of flasks, one containing vermiculite and one containing resin, were washed onto sieves using fine streams of water. The sieving action was continued until 600 ml. of water had been expended on each sample. The beakers receiving the KTPB were replaced, and the sieving was resumed for an additional 200 ml. of vehicle.

KTPB recovered in each sieving interval was concentrated by evaporating the sieving vehicle. The KTPB was then hydrolyzed by aqua regia, and its hydrolyzate was analyzed for K. The results of this experiment are presented in Table 7.

Table 7. Removal of KTPB from exchange materials through sieving

Sieving vehicle	Volume of vehicle used (ml.) 1st sieving	2nd sieving	Exchange material	Removal of KTPB (%) 1st sieving	2nd sieving
Water	50	80	Resin	81.7%	0.0%
Cyclohexane	50	80	Resin	61.6%	0.0%
Water	600	200	Resin	75.9%	0.5%
Water	600	200	Vermiculite	89.2%	0.6%

More KTPB was separated from the resin by sieving than by dissolving it in acetone. It is, however, apparent that continued sieving by water cannot, under the above conditions, free KTPB quantitatively from Na-IR-120. That some

of the K from the KTPB must have gone on the exchange sites of these materials was shown by the fact that a leaching of the resin systems by acetone subsequent to the second sieving with water recovered no additional K from the system. Lower results were obtained with cyclohexane, because this vehicle caused the resin and KTPB particles to clump together, thus making the removal of the KTPB difficult.

From these considerations it is apparent that the low recovery of KTPB from exchange materials can be partially overcome by separation of undissolved KTPB. However, the above sieving method cannot be used to obtain quantitative recovery of KTPB from exchange materials.

Separation by partitioning

Another method of separating KTPB from exchange materials lies in the partitioning of KTPB from an aqueous system containing the cation exchanger to an organic solvent phase. By this means the KTPB would be removed from the cation exchanger without having contacted the exchanger in an ionized form. Any salt present would be more soluble in the water phase than in the organic solvent phase. Therefore, the organic solvent phase containing the KTPB would be relatively free of the salt.

To determine the actual partitioning of KTPB from an aqueous system to an organic solvent, six solvents were

selected for study--three polar solvents (ethyl acetate, isobutyl alcohol, and benzyl alcohol) and three relatively non-polar solvents (cyclohexane, carbon tetrachloride, and benzene). To 50-ml. test tubes there were added 5 mg. of K (KCl) and 90 mg. of NaTPB in 8 ml. of water. To each test tube a known amount of solvent, approximately 20 gm., was then added. The test tubes were then stoppered and shaken end over end for 2 hours. The solutions within the test tubes were allowed to separate into separate phases, after which the organic phases were measured and analyzed for total K. The K recovered in the organic phase is reported in Table 8.

Of the six solvents tested, only the polar solvents offered any promise. Ethyl acetate, the most efficient

Table 8. Amount of KTPB partitioned to an organic solvent phase during the shaking of an aqueous phase containing KTPB with an organic solvent phase

Solvent	Weight of solvent (gm.)	Recovery of added K (%)
Cyclohexane	20.0	0.0
Carbon tetrachloride	20.0	0.0
Benzene	21.0	0.9
Ethyl acetate	20.5	37.7
Isobutyl alcohol	20.0	8.7
Benzyl alcohol	20.2	19.8

solvent, was tested further.

In devising additional tests for the partitioning of K into an ethyl acetate phase, Na-IR-120 was introduced as a competitor for any K ionized through the action of ethyl acetate. Morgan's solution was added to increase the miscibility of the aqueous phase with the ethyl acetate, thereby aiding the partitioning process, and to compete with any K ions for exchange sizes on the IR-120 resin.

There were added to 125-ml. Erlenmeyer flasks the following materials: 6.00 mg. K (KCl); 102 mg. NaTPB; 10 ml. 2 N Morgan's solution; 3.00 g. Na-IR-120; 13 ml. water; 25 or 100 ml. ethyl acetate. Some flasks were shaken on a wrist shaker for 2 hours, while others were allowed to stand 24 hours with only an occasional swirl so slight as not to allow contact between the ethyl acetate and the resin. In each case the ethyl acetate was then decanted, followed by the supernatent aqueous phase. Finally, the KTPB-resin was washed by 10 to 15 ml. of water. The combined filtered solutions were then analyzed for total K. Results of these non-duplicated determinations are given in Table 9.

To study the effect of consecutive extractions involving decantation and replacement of the ethyl acetate layer, there were added to 50-ml. test tubes the same amounts of ingredients as were added to the flasks above, with the exception that 20 ml. of ethyl acetate were used instead of the 25 or

Table 9. Amount of KTPB-K partitioned to ethyl acetate from an aqueous phase containing KTPB, Na-IR-120, and Morgan's solution

Vessel	Volume of ethyl acetate (ml.)	Agitation	Recovery of added K (%)
Flask	25	Shake	32.8%
Flask	100	Shake	33.3%
Flask	25	Swirl	41.1%
Flask	100	Swirl	36.8%
Test tube	20,20,20	Shake	13.9%

100 ml. used above. The samples were shaken on a wrist shaker for 2 hours, without there being any contact between the ethyl acetate phase and the resin. Over 90% of the ethyl acetate layer was decanted and an additional 20 ml. of fresh ethyl acetate was added. The shaking and decanting process was repeated twice. After the third decantation the remainder of the ethyl acetate layer was pipetted off and the combined ethyl acetate layers were analyzed for K. The K recovered by this method is also shown in Table 9.

As can be seen from Table 9, it does not appear that K can be efficiently recovered through partitioning with ethyl acetate.

Influence of added cations

While the removal of KTPB from the resin by sieving was not quantitative, it was adequate (81.7% and 75.9%) to indicate that the 50% recovery obtained through leaching of a KTPB-resin system with acetone could be markedly improved upon. Since a major difficulty in the removal of dissolved KTPB from the resin lay in the attraction of K to the exchange positions, the next approach to the removal of KTPB involved the use of large concentrations of cations to compete with dissolved K for exchange sites. A large cation concentration should be effective when applied in single acetone extraction studies and should be even more effective in leaching studies, in view of the continuous renewal of K-free extractant during leaching. To evaluate the use of high salt concentrations in the removal of KTPB-K from resin, the following experiment was conducted.

Ten ml. of a 1000 ppm K solution (0.26 me. K as KCl) and 5 ml. of a 3% NaTPB solution (0.44 me.) were added to 125-ml. flasks. To four sets were added five drops of 3 N HCl (0.6 me.); to the fifth set no HCl was added. Weighed amounts of H-IR-120 (0.2 to 0.4 gm.) were added to the flasks, followed by 5 ml. of salt solution in the case of the first four sets of flasks.

To each flask in the first four treatments 20 ml. of acetone were added. The flasks were swirled for 1 minute

before filtering the contents through medium-porosity sintered glass Buchners and washing with two 2-ml. portions of 1:1 acetone-N acetate. Treatment 4 was an exception in that washing was by acetone-water rather than by acetone-N acetone.

The contents of the flasks in treatment 5 were filtered through sintered glass Buchners. The resin-precipitate residue in the Buchner was leached with 5 ml. of N NH_4OAc added to 20 ml. of acetone, followed by two 2-ml. portions of 1:1 acetone-N NH_4OAc.

The combined filtrate-wash from each of the five treatments were analyzed for K. The results are reported in Table 10. The percentages of the total cation concentration that

Table 10. Removal of KTPB-K from exchange resin as influenced by amount and method of salt addition

Salt treatment	Cations in solution initially*(%)	K removed (%)
1. 20 me. NH_4OAc in extract and 2 me. in wash	95.1	95.8
2. 20 me. NaOAc in extract and 2 me. in wash	94.6	95.3
3. 5 me. NaOAc in extract and 2 me. in wash	83.9	88.8
4. 20 me. NH_4OAc in extract	92.0	88.7
5. 5 me. NH_4OAc in leaching solution and 2 me. in wash	--	95.3

*Percentage of total cations (soluble + exchangeable) in solution in initial system.

was in solution (as contrasted to that on the resin exchange sites) in the initial system are also given in this table for comparison.

In this experiment the existence of a predictable relationship between the salt concentration used in an equilibrium extraction and the K removed has been established. Thus, one can achieve the efficiency of KTPB-K removal desired by adding an appropriate amount of salt to the KTPB-acetone-resin system.

K was removed more efficiently in this experiment when the resin was leached. Thus, it appears that this method should be preferred. However, the rate of solution of KTPB must also be considered. In the leaching of certain systems the acetone contact with the precipitate may be poor, resulting in inefficiency of extraction of KTPB. In these cases shaking with acetone will be required in order to effect solution of the precipitate.

With IR-120 it has been necessary to add considerable amounts of salt to the extraction system to ensure near quantitative release of the K present as KTPB. With vermiculite the exchange capacity and the rate of exchange are such as to allow the use of much lower salt concentrations, as has been shown in the following determination.

Twenty ml. of a KTPB-bearing solution of 0.5 N to Morgan's solution and containing 50% acetone (by volume) were shaken with 0.5 gm. of vermiculite for 12 minutes. The system was

filtered and washed with 1:1 acetone-water. Analysis of the filtrate indicated a recovery of 94.7% of the added K. This near quantitative recovery of K by the use of a moderate amount of salt (10 me.) indicates that reasonable removal of KTPB-K from most exchange materials may be accomplished through equilibration in acetone solution containing from moderate to high salt levels. This does not preclude the possibility that higher salt concentrations may be needed to compete with K ions for sites on highly degraded micaceous minerals.

Degradation of Soils and Micaceous Minerals

Degradation experiments were initiated soon after a quantitative method for determining K in KTPB was available, even though the optimum conditions for handling TPB compounds in soils and micaceous minerals had not yet been established. This was done to evaluate the usefulness of NaTPB in this application and thus to determine if further investigation was warranted. Also, these experiments were designed to evaluate the effect of temperature, pH, and other experimental conditions on the degradation process as a whole. The results of these experiments, therefore, provided a guide in the development of optimum conditions for the use of TPB compounds in these materials.

Leaching with NaTPB

One method of degrading micaceous minerals with NaTPB involves leaching of the material with a dilute solution of NaTPB. NaTPB, like other salts, dissociates in water. Therefore, in leaching with NaTPB the Na ion would effect some replacement of K from the minerals. The displaced K may, however, be precipitated as KTPB, depending on the concentration of TPB ions in the solution. According to Geilmann and Gebauhr (25) the solubility of KTPB in water is 53 mg. per 1. The maximum rate of K removal by an aqueous leaching solution should therefore be 5.8 mg. of K per 1. As the concentration of TPB ions in the solution is increased, the solubility of KTPB is decreased until, in a 0.3% NaTPB solution (3000 ppm NaTPB), K is soluble only to the extent of 0.1 mg. per 1. Therefore, the NaTPB concentration used to leach micaceous minerals should not exceed 3000 ppm NaTPB.

One-gm. samples of air dry South Carolina vermiculite, containing 27.1 mg. of K, were leached with NaTPB solutions to evaluate the use of NaTPB as an extracting salt. In one experiment the vermiculite samples were placed on filter paper in conical funnels and leached at the rate of 1 l. per day for 1 week with 60 ppm (0.00018 N), 240 ppm (0.00070 N), and 3000 ppm (.0088 N) NaTPB solutions. For comparison, samples were also leached with 0.02 N Morgan's solution and a 60 ppm

NaTPB-0.02 N Morgan's solution. In one case, to increase the solubility of KTPB in the leaching solution, 1% acetone by volume was incorporated in a 240 ppm NaTPB solution. Data presented elsewhere (Figure 2) indicate that this increase in solubility was slight. The results of this experiment are given in Table 11.

Table 11. Amount of K leached from South Carolina vermiculite by dilute NaTPB solution

Leaching solution	Cumulative amount of K removed (mg.)				
	1 day	2 days	3 days	5 days	7 days
60 ppm NaTPB	0.22	0.31	0.38	0.48	0.56
60 ppm NaTPB-0.02 N Morgan's	0.45	0.49	0.53	0.64	0.71
0.02 N Morgan's	0.41	0.44	0.47	0.53	0.57
240 ppm NaTPB	0.33	0.46	0.57	0.71	0.84
240 ppm NaTPB-1% acetone	0.31	0.42	0.52	0.67	0.81
3000 ppm NaTPB	0.00	0.00	0.00		

In 1 day the 240 ppm NaTPB solution removed nearly as much K from the vermiculite as the Morgan's solution even though 14 times as much Na was leached through the sample in the case of the Morgan's solution. When the time of reaction was extended to 7 days, the 240 ppm NaTPB solutions removed considerably more K than did the Morgan's solution. It should

be noted that the 1-gm. vermiculite samples contained 0.18 mg. of exchangeable K as determined by leaching with neutral N NH_4OAc. Therefore, these Na solutions removed not only the so-called "exchangeable K" but some of the non-exchangeable as well. As the amount of non-exchangeable K removed increased, the NaTPB solutions were progressively more effective in their removal of K than the Morgan's solution. This suggests that the TPB ions in the NaTPB solutions in some manner reduced the interfering effects of the replaced K on the continued removal of K.

The amount of K removed increased as the NaTPB concentration increased from 60 ppm to 240 ppm because there were more Na ions present at the latter concentration to replace the K. For the same reason more K was removed when the Na concentration was increased by mixing Morgan's solution with the 60 ppm NaTPB. On the other hand, when the NaTPB concentration was increased to 3000 ppm, there was no K in the filtrate. At this concentration the replaced K was apparently precipitated. While the amount of K extracted (up to 0.84 mg. K) was not comparable to the amounts extracted in later degradation experiments, this mild leaching method appears promising because of the progressive removal of considerable amounts of non-exchangeable K.

Degradation with concentrated salt solutions

In the degradation of micaceous minerals NaTPB may be added to precipitate the K as it is replaced from the minerals so that the displaced K will not interfere in further replacement of non-exchangeable K. The actual replacement of the K, however, depends upon the presence of replacing cations that cause an expansion of the crystal lattice. Na is such a cation, but the concentration of Na in the NaTPB used to precipitate the K is quite small. Therefore, a salt solution should be used in the degradation of the micaceous minerals.

Even in the absence of NaTPB it is known that the replacement of non-exchangeable K depends upon the ratio of K to replacing cation in the extracting solution. An increase in the concentration of replacing cations effects an increase in the amount of K replaced. Therefore, the degradation of micaceous minerals with NaTPB should be increased by the use of high salt concentrations. To test the validity of this assumption the following experiment was conducted.

Two-gm. samples of air dry South Carolina vermiculite were added to 50 ml. of solutions that were 4N to NaOAc, 6N to NaCl, 6N to $MgCl_2$, or salt-free. One-half of the solutions contained 0.85 gm. of NaTPB, which was 1.7 times the amount needed to precipitate the 54.2 mg. of K in the 2 gm.

of vermiculite. The rest of the solutions were free of NaTPB.

These systems were incubated at 70° C. for a period of 9 hours and then for a period of 30 days. At the end of each period the solutions were cooled and 50 ml. of acetone were added. The flasks were swirled to dissolve the KTPB in the resulting 1:1 acetone-water solution, and the solutions were then filtered through Whatman 42 filter paper on porcelain Buchner funnels. The residue in each case was washed with 5 ml. of a 1:1 acetone-N salt solution, followed by 50 ml. of water. The K in the filtrate was determined by hydrolysis with aqua regia. The vermiculite residue from the 9-hour degradation period was then degraded for 30 days at 70° C. in another 50 ml. of the same salt solution used above, and the K removed was determined as before. The amount of K removed per oven-dry gm. of vermiculite is given in Table 12.

When no salt was present, the NaTPB removed K surprisingly well over the long contact period. The addition of NaTPB alone constitutes the mildest degradation treatment, yet nearly one-half of the total K in the vermiculite was removed. In the case of soils, an addition of NaTPB alone would cause little disturbance to its natural status other than its K distribution. Therefore, this method may be useful in assessing the long-time K-supplying power of soils.

The concentrated salt solutions containing NaTPB removed more K from the vermiculite than did the solutions containing

Table 12. Degradation of South Carolina vermiculite with concentrated salt solutions and NaTPB

Salt solution	Amount of NaTPB added (gm.)	K removed (mg. per gm. of vermiculite) 9-hour period	30-day period	Total
6N $MgCl_2$	0.85	10.13	4.64	14.77
	0.00	1.85	5.34	7.19
6N NaCl	0.85	14.15	4.42	18.57
	0.00	4.10	6.02	10.12
4N NaOAc	0.85	15.60	4.24	19.84
	0.00	1.83	2.52	4.35
No salt	0.85	6.02	7.39	13.41
	0.00	0.05	0.06	0.11

no salt or those containing no NaTPB. The effect of the salt is most evident in the initial rapid rate of K removal. Thus, it would appear that salt should be added to a NaTPB solution in order to maximize degree and speed of degradation of micaceous minerals.

Na was a more effective replacing cation than Mg. While the 6N NaCl and 6N $MgCl_2$ solutions extracted much more K from the vermiculite than did 4N NaOAc, the NaOAc-NaTPB system extracted more K than did either the NaCl-NaTPB or the $MgCl_2$-NaTPB system. Consequently, NaOAc and Morgan's (NaOAc-HOAc) solutions were used frequently in subsequent degradation experiments with NaTPB.

Degradation as a function of time

It is to be expected that the time of degradation is an important factor in the removal of K, since the replacement of K from interlayer positions of fairly large particles is involved. The results of the preceding experiment support this idea. Theoretically, if the action of NaTPB through the precipitation of replaced K is valid, the amount of K removed should be the same whether single or successive extractions are used, as long as the total time involved is the same. The following experiment was carried out to determine the validity of these concepts.

Two-gm. samples of air dry vermiculite were added to flasks containing 50 ml. of a 2N NaOAc solution. To one-half of the flasks were added 25 ml. of a 3.4% NaTPB solution, and to the rest 25 ml. of water were added. After mixing, these systems were incubated at 70° C. for different lengths of time. At the end of the degradation period 75 ml. of acetone were added to dissolve the KTPB precipitate. The K in solution was determined by the procedure used in the preceding experiment.

In most treatments the same vermiculite sample was degraded successively. In these cases the degraded residue from one degradation period was dried free of acetone, added to 75 ml. of a solution identical to that used previously,

and degraded for another period. The cumulative amounts of K removed from the vermiculite by the single and successive degradations are shown in Table 13 and Figure 3.

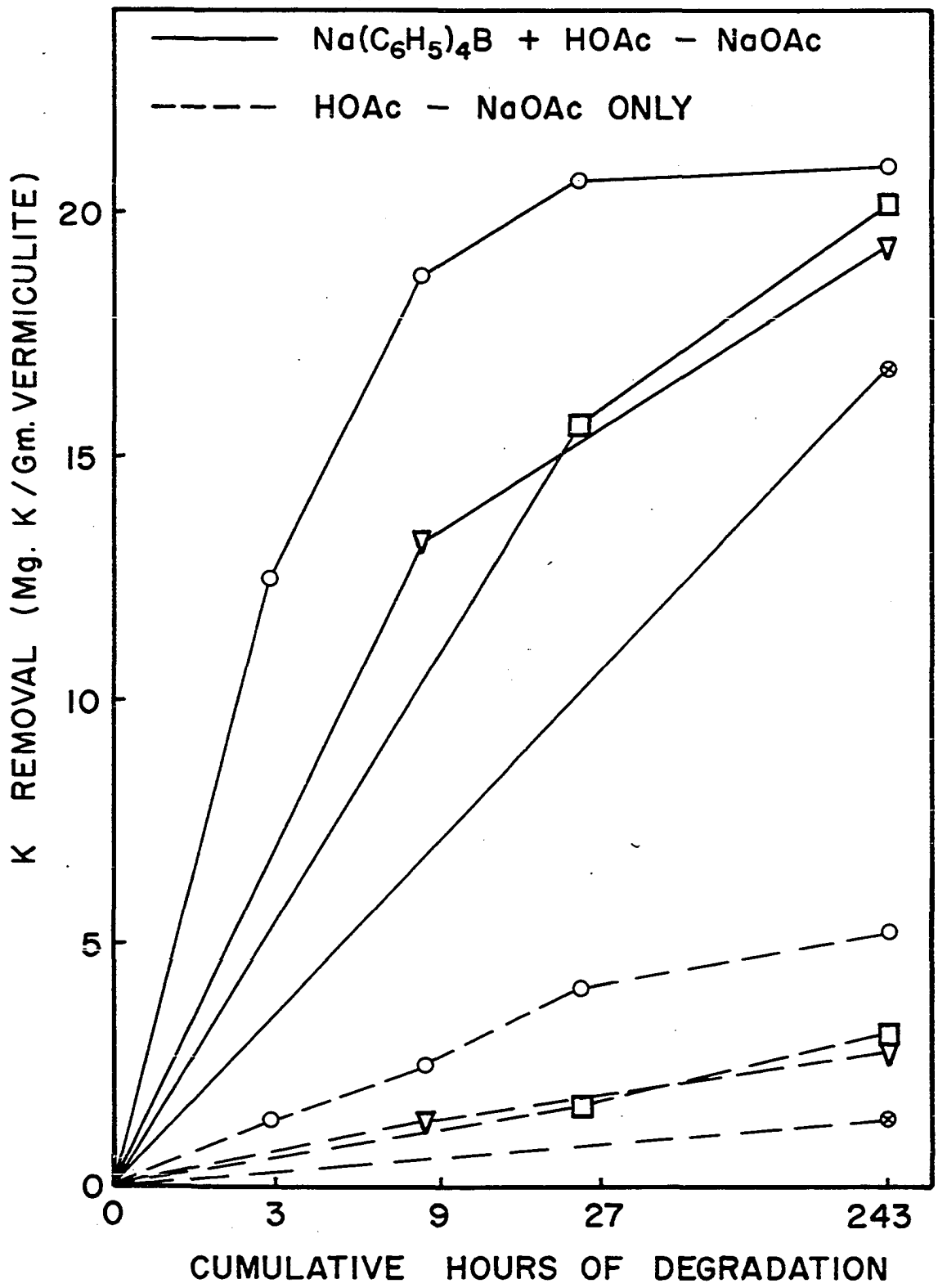
When the NaOAc was used without NaTPB, there was little effect of time or previous extraction history on the amount

Table 13. K removed from South Carolina vermiculite as a function of degradation time

Amount of NaTPB present (gm.)	Cumulative amount of K removed (mg. per gm. of vermiculite) Total period of degradation			
	3 hrs.	9 hrs.	27 hrs.	243 hrs.
0.85	12.50	18.66	20.61	20.96
0.00	1.31	2.48	3.98	5.17
0.85		13.08		19.35
0.00		1.38		2.77
0.85			15.59	20.24
0.00			1.69	3.04
0.85				16.92
0.00				1.43

of K removed by a single extraction. For instance, the K removed in 3 hours and 243 hours was 1.31 mg. of K and 1.43 mg. of K, respectively, per gm. of vermiculite. When this much replaced K accumulated in the extracting solution, further replacement of K was prevented even though there were 100 me. of Na and less than 0.1 me. of K in the solution.

Figure 3. K removal in single and successive degradations of vermiculite by HOAc-NaOAc and $Na(C_6H_5)_4B$-HOAc-NaOAc solutions


Na(C6H5)4B + HOAc – NaOAc
HOAc – NaOAc ONLY
K REMOVAL (Mg. K / Gm. VERMICULITE)
0
5
10
15
20
0
3
9
27
243
CUMULATIVE HOURS OF DEGRADATION

These results emphasize the importance of preventing the accumulation of replaced K in the extracting solution when the removal of non-exchangeable K is desired.

When the accumulation of replaced K was partially reduced by degrading the same sample of vermiculite successively with fresh salt solutions, the NaOAc removed more K than it did in a single degradation for the same period of time. As the number of successive degradations during a given time interval increased, the total K removed increased. The amount of K removed by NaOAc was also increased when NaTPB was added to the NaOAc. In each case, the increase in K removal was due to a decrease in the interference from K in the extracting solution. The use of successive degradations was only partially effective in this regard. The NaTPB addition was much more effective.

Contrary to expectations the NaOAc-NaTPB solutions did not remove the same amount of K in a single degradation as they did in successive degradations over the same period of time. More K was removed by the successive degradation method.

The amount of K removed by the NaOAc-NaTPB solutions in a single degradation increased as the time of degradation was increased. This suggests that the amount of K removed was determined by the rate of K replacement from the interior of the large vermiculite particles. However, the same rate of

replacement should be operative in the successive degradations and should therefore limit the K removed by successive degradations in a 243-hour period to the same value as that removed by a single degradation for the same period. Since this did not occur, other factors must be involved.

It is possible that more K was removed by the successive degradation for 243 hours than by the single extraction for this period of time because there was still some effect from K in the extracting solution on further K removal even though NaTPB was present. In this event, either there was some decomposition of the NaTPB during the degradation period, or there was not enough excess TPB ions added to remove all of the K from solution.

The amount of NaTPB added was 1.7 times the amount needed to precipitate all of the K in the vermiculite. Experiments on the stability of NaTPB (Table 5) indicated that it was relatively stable under the temperature and pH conditions used in this experiment. Furthermore, the increase in K removed as the single degradation period was increased from 27 to 243 hours indicates that an excess of NaTPB was still present. Therefore, it is not readily apparent how soluble K could be present to be causing this effect.

Another possible explanation for the difference in recovery between successive extractions and a single extraction

for a given degradation period may be found in the efficiency of removal of KTPB from the degraded vermiculite. In the previous section on the separation of KTPB from exchange systems it was observed that the solution of KTPB in the presence of non-degraded vermiculite results in the loss of some dissolved K to vermiculite. Under the salt concentration conditions prevailing here one would anticipate a loss of about 2% to 5% of the KTPB dissolved in each step, provided the vermiculite had not been degraded. In the presence of degraded vermiculite the loss of dissolved K may be higher. K lost to vermiculite in one acetone extraction would be recovered in a subsequent extraction, provided successive extractions are used. The overall loss of dissolved K to the degraded vermiculite exchange sites would then be less when a successive extraction method is used than when a single extraction is used. Therefore, part of the difference in the amount of K removed by the two methods observed in this experiment may be due to a difference in efficiency of removing KTPB.

The vermiculite contained a total of 28 mg. of K per gm. Therefore, in 243 hours, 74.9% of the naturally occurring K was removed. Since much of the K present in the sample must be lattice K in the biotite found therein, release of this large an amount of the total K indicates that the degradation method has marked possibilities.

Degradation as a function of temperature

The rate of K replacement from interlayer positions in micaceous minerals will depend upon the temperature of the system. For this reason the preceding degradation experiments had been conducted at 70° C. As the temperature is increased, the rate of replacement should increase. Therefore, an experiment was carried out with boiling salt solutions to determine whether higher temperatures were desirable for the degradation of micaceous minerals. To maintain a relatively constant volume of extracting solution the systems were refluxed.

Two-gm. samples of air-dry South Carolina vermiculite were added to flasks that contained either 100 ml. of 2N NaOAc and 1.5 gm. of NaTPB or 66 ml. of 2N NaOAc and 1 gm. of NaTPB. These systems were refluxed for a period of 20 hours. The solution volume was doubled by the addition of acetone, the KTPB was dissolved by swirling, and the K in solution was determined by the same procedure as was used in the preceding degradation experiments. The K removed was 17.5 and 17.7 mg. of K per gm. of vermiculite.

The degraded residue was dried free of acetone and then refluxed again for 6 hours in 60 ml. of a 2N NaOAc solution which contained 0.6 gm. of NaTPB. The K removed was determined as before and found to be 3.1 and 2.1 mg. of

K per gm. of vermiculite, respectively. Thus the total K removed in 26 hours by two successive reflux treatments was 20.6 and 19.8 mg. of K per gm. of vermiculite.

While a direct comparison of these results with those obtained at 70° C. in the same time and with the same number of successive extractions is not possible, it is apparent that the degradation is more rapid at the boiling temperature. After 20 hours of refluxing, 17.5 mg. of K per gm. of vermiculite were removed, as compared with 15.59 mg. in 27 hours at 70° C. The total removed, however, was again about 20 mg. of K, which is comparable to the maximum removed by the various treatments at 70° C. It appears that the last 8 mg. of K per gm. of vermiculite are very difficult to remove.

The K removed by 20 hours of refluxing was not affected by increasing the NaTPB present by 50%. The 1-gm. addition of NaTPB was four times the amount needed to precipitate all of the K in the vermiculite. However, in view of later observations that the NaTPB is unstable at boiling temperatures (Table 5), an increase in K removed might have been expected from an increase in NaTPB addition. Despite the instability of NaTPB at this temperature, this method of degradation appears quite rapid and effective.

Degradation of large vermiculite samples

In many investigations of K and NH_4 fixation a K-free expanded micaceous mineral would be very useful. In the present study, for instance, such a mineral could be used to develop methods of precipitating and recovering added K from a K-fixing micaceous mineral. If there were no naturally occurring K in the mineral, a quantitative check on the recovery by a given method could be made against the known amount of K added.

Practically all of the micaceous minerals available for fixation studies contain some K. The South Carolina vermiculite used in these experiments, for instance, is a vermiculite-biotite mixture, which contains lattice K. The previous degradation experiments, however, indicate it might be possible to remove all of this K with a salt solution and NaTPB. Therefore, an attempt was made to prepare a bulk sample of K-free vermiculite.

Two 125-gm. samples of South Carolina vermiculite were placed in flasks with 525 ml. of 4N NaOAc and 37.5 gm. of NaTPB. These systems were incubated at 95° C. for 20 hours. The solutions were cooled and acetone was added to double the volume of solution. The solutions were swirled to dissolve the KTPB and then allowed to stand for settling. The supernatant liquid was decanted through a Whatman 42 filter paper. The residue was washed twice with 300 ml. of acetone, and the

acetone was then decanted through the filter paper. Finally, the residue was transferred to the filter paper and washed with two 50-ml. portions of acetone, followed by two 50-ml. portions of water. The K in the filtrate was determined by hydrolyzing with aqua regia, as in the other degradation experiments.

The air-dried degraded residues were refluxed for 15 hours in 375 ml. of 2N NaOAc that contained 9 gm. of NaTPB. The K removed from the vermiculite was separated from the vermiculite as before and determined.

The air-dried residues from the second period of degradation were refluxed again for 20 hours in 350 ml. of 2N NaOAc that contained 10 gm. of NaTPB. The individual results obtained in these successive degradation experiments with bulk samples of vermiculite are given in Table 14.

The total K removed in this experiment was only 13.2 mg. and 12.2 mg. of K per gm. of vermiculite. These values are

Table 14. K removed in the degradation of large samples of South Carolina vermiculite

Degradation treatment	K removed (mg. per gm. vermiculite)	
	Sample 1	Sample 2
20 hours at 95° C.	5.2	4.7
15 hours refluxing	5.3	5.1
20 hours refluxing	2.7	2.4
Total	13.2	12.2

quite low compared to the more than 20 mg. of K removed in the preceding degradation experiments, even though the vermiculite was exposed to high temperatures for longer periods of time. In the case of large vermiculite samples, however, the solution volume per gm. of vermiculite and the amount of excess NaTPB were smaller. This may account for the inefficient removal of K observed.

From the visible persistence with which the white KTPB precipitate remained when the degraded vermiculite was treated with acetone it was apparent that KTPB is not readily removed from large vermiculite samples. The degraded residues were given a rigorous treatment with acetone, but the low results obtained for K removal may still have been due in part to incomplete removal of the KTPB.

It is apparent from the results of this experiment that it will be difficult to prepare a bulk sample of K-free micaceous mineral.

Degradation of soils and micaceous minerals

South Carolina vermiculite was used in all of the experiments that were carried out to develop methods of using NaTPB in the degradation of micaceous minerals. It was also important to determine how effective NaTPB would be in the removal of K from soils and other micaceous minerals. Therefore, a degradation experiment was carried out with muscovite, illite

(Grundite), and two surface soil samples (Fayette and Carrington) using the methods available at the time, even though they probably did not provide the optimum conditions for the removal of K. South Carolina vermiculite was used in this experiment also for comparative purposes.

Three-gm. samples of these materials were placed in flasks containing 40 ml. of 2N Morgan's solution. One-half of these flasks also contained 0.68 gm. of NaTPB. These systems were successively incubated for a 2-hour period, an 8-hour period, and a 12-hour period at 70° C. They were then incubated at room temperature for 60 days. At the end of each degradation period acetone was added to double the solution volume, the KTPB was dissolved by swirling, and the K in solution was determined in the same manner as in the other degradation experiments. The degraded residue was dried free of acetone and degraded again in 40 ml. of the same solution that was used in the preceding degradation period. The mean values of duplicate determinations are given in Table 15.

More K was removed from the micaceous minerals and the Fayette soil by the NaTPB-Morgan's solution than by the Morgan's solution. In these cases the difference in amount of K removed by the two solutions increased progressively as the time of degradation increased.

Practically all of the K in muscovite is lattice K, yet

Table 15. K removed in successive degradations of different soils and micaceous minerals with Morgan's solution and NaTPB

Sample	Degradation with(w) or without(w/o) NaTPB	K removed (mg. per gm. vermiculite) First 2 hrs. at 70° C.	Next 8 hrs. at 70° C.	Next 12 hrs. at 70° C.	60 days at room temp.	Total
Muscovite	w	1.14	0.19	0.53	7.64	9.50
	w/o	0.56	0.07	0.09	0.18	0.90
South Carolina vermiculite	w	4.28	8.09	7.76	8.06	28.19
	w/o	0.45	0.42	0.38	*	
Grundite	w	6.35	2.09	1.21	3.54	13.19
	w/o	1.70	*	0.92	3.87	
Fayette soil	w	0.52	*	0.63	0.59	
	w/o	0.13	0.03	0.01	0.07	0.24
Carrington soil	w	0.14	*	0.01	0.02	
	w/o	0.12				

*The material was degraded for this interval but the K removed was not determined.

10.9% of the total K in the mineral was removed. Illite is a dioctahedral mineral like muscovite, and it also contains mainly lattice K. The total K removed from the illite by this degradation procedure, however, amounted to 33.8 me. K per 100 gm. This method of removing K from the contracted lattice of micaceous minerals is therefore applicable to the dioctohedral minerals, as well as the trioctohedral minerals such as vermiculite and biotite.

The results obtained with South Carolina vermiculite in this experiment are not entirely consistent with the results obtained in other degradation experiments. In a previous experiment in which this vermiculite was degraded successively for a total period of 243 hours it appeared that K removal in excess of 21 mg. may not be possible (Figure 3). That is, the K removal was not increased appreciably by degrading a sample a fourth time for 216 hours. In the present experiment, however, all of the 28 mg. of K in each gm. of vermiculite were removed. Since the degradation was continued for more than 60 days in this experiment, it is possible that the difficulty involved in removing the last increments of K present is that considerable time is needed for the replacement of K deep in the interior of the particles.

The limited data obtained with the two soils indicate that NaTPB can be used to differentiate between soils in regard to their ability to release K. The Fayette and Carrington soils contained nearly the same amount of exchangeable K as determined by Morgan's solution. When the NaTPB-Morgan's solution was used instead of Morgan's solution alone, additional K was removed from the Fayette soil but not from the Carrington soil. That is, the Fayette soil released K that is not normally exchangeable, whereas the Carrington did not. Furthermore, the Fayette soil continued to release appreciable amounts of K to the NaTPB-Morgan's solution over

the entire period of degradation. These results are consistent with the difference in the K-supplying power of these soils (43).

GENERAL DISCUSSION AND CONCLUSIONS

K in KTPB can be determined quantitatively either by dry ashing the KTPB in a platinum crucible at 400° C. or by wet ashing the KTPB in aqua regia. While these methods are quantitative, neither is entirely satisfactory for extensive degradation studies. The dry ashing method is simple, but its use is limited to a few small samples because of the platinum required. The aqua regia method, though long and tedious, is the best method available at present.

It has been reported in the literature that the TPB in KTPB can be quantitatively determined by its reaction with $AgNO_3$ or $HgCl_2$. The equations presented for these reactions indicate that the K would then be free, and that it could be removed in an aqueous solution and determined. However, it was not possible to obtain quantitative recovery of the K in KTPB by this means. The reason for the low recovery of K with these methods is still unknown. It does not appear that these methods should be given further consideration in the development of simpler and faster methods for the analysis of K in KTPB.

Only the method of determining K in KTPB by the use of cation exchange resins offered possibility of a simple and rapid, yet quantitative, method. The 97% recovery obtained in this study would be adequate in many cases. It is pos-

sible that the K recovery may be even better if the solution were equilibrated with a sample of resin, instead of being leached through a column. This method deserves further consideration, even though its use requires prior removal of large concentrations of salts used to hasten the replacement of K during degradation.

KTPB was not quantitatively removed from exchange materials by either sieving or partitioning methods. On the other hand, KTPB was dissolved and quantitatively separated from these materials by acetone-water solution. In most procedures a 50% acetone solution, which dissolves 10 mg. of KTPB per ml., was found to be adequate.

The KTPB solubility increases rapidly as the acetone concentration in acetone-water solution is increased beyond 50%. Therefore, the solution of large amounts of KTPB would be accomplished more efficiently through the use of solutions containing more than 50% acetone. In the case of large amounts of KTPB precipitate, it has also been found that solution by shaking with acetone is much more effective than is solution through leaching.

The success in using NaTPB to degrade micaceous minerals depends on the selection of experimental conditions that are conducive to both the precipitation of KTPB and the replacement of K from the micaceous mineral. Little difficulty in this regard was encountered in the choice of the proper pH

to be used. Both the K replacement and the K precipitation processes are favored by the use of acid solutions. The degree of acidity is limited, however, by the pH at which some destruction of the lattice occurs. A pH of 4.8 at low temperature has proven satisfactory in this work.

The choice of temperature was a difficult one. The rate of K replacement is increased by an increase in temperature, while the stability of NaTPB is decreased by this temperature rise. It appears that a temperature of over 70° C. should not be used. In fact, where it is practicable, micaceous minerals should be degraded at room temperature. If a short but rapid degradation is desired, the sample may be refluxed. Part of the difficulty arising from the instability of the TPB compounds at refluxing temperature may be overcome by the use of excess precipitatnt. At the same time, the pH of the solution should be increased from 4.8 to 7.

One of the most important factors in the degradation of micaceous minerals is the replacing cation in the extracting solution. It is essential that this cation be able to cause the mineral lattice to expand. That is, it can not be a fixable cation. Na appears to be satisfactory for this purpose. At least, it replaces K more effectively than does Mg.

A high concentration of replacing cation in the extracting solution is needed during the degradation to cause the replacement of K from the micaceous mineral. A high concen-

tration of replacing cation is also needed in the acetone-water solution that is used to dissolve and remove the KTPB.

When KTPB in a KTPB-resin-salt system is dissolved in acetone, it ionizes, and the K then brought into solution is attracted to the exchange sites of the resin until the ratio of soluble to exchangeable K approximates the ratio of total soluble to total exchangeable cations. If a large amount of replacing cation is present in the system, the ratio of total soluble to exchangeable cations is high and hence, the ratio of soluble K to exchangeable K is high. In this event most of the K is then removed with the acetone solution. The amount of replacing cation that must be added will depend on the number of exchange sites in the system. It was found with vermiculite and Amberlite IR-120 that a ratio of total soluble to exchangeable cations of 20 to 1 was adequate to remove over 90% of the K added as KCl.

In a degraded vermiculite system containing K and Na ions the K ion is preferentially adsorbed. Hence, the effectiveness of Na in preventing the loss of soluble K to exchange positions should be reduced accordingly. It has been suggested that loss of dissolved K on extraction of KTPB from degraded vermiculite by acetone may be sufficient to cause considerable inefficiency in vermiculite degradation by single extraction.

Salt solutions containing NaTPB removed more K from

soils and micaceous minerals than did salt solutions alone. The original proposal, that the removal of soluble and exchangeable K by precipitation would increase the amount of K removed, was substantiated. Thus, the non-exchangeable character of the K in the micaceous minerals depends on the presence of K (or other fixable cations) in the extracting solution. Any general designation of K in micaceous minerals as "non-exchangeable" is open to question. Only by careful description of the method used can it be said that the K not removed was non-exchangeable. Even then it must be added that the K was non-exchangeable only under the conditions employed in the method.

The soils released K to NaTPB-Morgan's solution in different degrees. The Fayette soil released large amounts of K and continued to release K for a considerable period of time when NaTPB was present to precipitate and thus inactivate the K released. The Carrington soil, on the other hand, released no more K to the NaTPB-Morgan's solution than it did to Morgan's solution alone. This difference in K release to NaTPB solutions is comparable to the difference Pratt (43) observed in their ability to supply K to plants. Accordingly, it may be possible to use NaTPB to determine the K-supplying power of soils.

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